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THE USE OF SELENOUREA IN ANALYTICAL CHEMISTRY

I. THE BEHAVIOR OF SELENOUREA TOWARD THE CATIONS OF THE HEAVY METALS AND THE COMPOSITION AND STABILITY OF THE SELENOUREA COMPLEXES OF BISMUTH

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Verneuil [1] was the first to prepare selenourea in 1886; he obtained compounds of selenourea with silver chloride, mercury chloride, and platinum chloride. We were unable to find any other published data on compounds of the metals with selenourea. We could not find information on the use of selenourea in analytical chemistry either. Selenourea, however, as our experiments showed, forms stable complexes with heavy metals just as thiourea does. The selenourea complexes formed with antimony, bismuth and a number of other metals, while being more intensely colored than the corresponding thiourea complexes, are also more stable. Results are given in the present article of studies on the interaction of selenourea with heavy-metal cations, and also on the study of the composition and stability of bismuth selenourea complexes.

1. A Study of the Behavior of Selenourea Toward Heavy-Metal Cations

Selenourea was synthesized according to Verneuil's method [1]. Since selenourea is readily oxidized by atmospheric oxygen, particularly in solution and in the light, it is necessary to keep it in the solid state, and, especially, store it in flasks of dark glass with close fitting stoppers. Neutral and alkaline solutions of selenourea readily decompose in the air with deposition of selenium. Acid solutions of selenourea store fairly well for a long time; thus, selenourea in 1 N nitric acid only starts to break down appreciably after two hours' standing in the air. Such a solution is suitable for qualitative reactions for 4-5 hours. For the work we carried out, we used solutions of selenourea in dilute nitric acid.

The behavior of heavy-metal cations toward selenourea was studied as follows: a 0.4 M solution of selenourea and 1 M solutions of heavy-metal salts were prepared. The solution of the metal salt was then allowed to react with the selenourea solution and the external effects observed. The following results were obtained:

Fe^{3+}. A rose-colored precipitate was formed which was soluble in water. The aqueous solution had a reddish yellow color.

Cu^{2+}. A white precipitate soluble in excess reagent was formed.

Bi^{3+}. A soluble, yellow-colored precipitate was formed; when excess reagent was used, a soluble complex with a red color was formed.

Hg^{2+}. A white precipitate soluble in excess reagent was formed.

Hg_2^{2+}. A black precipitate which was obviously mercury metal was formed.

Pb^{2+}. A crystalline, pale yellow precipitate was formed which was insoluble in excess reagent.

Ag^{+}. A white precipitate soluble in excess reagent was formed.

Sn^{2+}. A pale-yellow, crystalline precipitate was formed which was soluble in excess reagent. The soluble complex had a yellow color.

Sn^{IV}. A soluble complex with a yellow color was formed.

$Sb^{III,V}$. The color intensity was considerably greater than in the case of tin.

$As^{III,V}$. A soluble compound with a weak yellow color was formed.

Pd^{2+}. A black precipitate was formed which was readily soluble in excess reagent to give a red-colored complex.

Au^{III}. A precipitate with a dirty yellow color was formed; this was soluble in excess reagent.

MoO_4^{2-}. This was reduced to molybdenum blue.

VO_3^-. This was reduced to quadrivalent vanadium; the solution was blue.

WO_4^{2-}. This was reduced to tungsten blue.

During the interaction of selenourea with the ions of divalent iron, trivalent chromium, nickel, cobalt, manganese, cadmium, and zinc, no external effects could be observed.

In order to establish the stability of the selenourea complexes of silver, copper, and mercury, experiments were carried out on the solubility of certain sparingly soluble salts of silver, copper, and mercury in a solution of selenourea. Experiments showed that the ions of silver, univalent copper, and divalent mercury readily dissolve in the selenourea solutions; this indicates a high stability for their selenourea complexes. Bismuth forms two complexes which are readily distinguished from each other: one with a yellow color when there is a small excess of selenourea, and the other with a red color when a large excess of selenourea is used.

2. A Study of the Composition of the Selenourea Bismuth Complexes

The composition of the bismuth selenourea complexes was determined by means of the Ostromyslenskii - - Job method [2, 3]. The property of the system studied was the optical density of the solution. It is clear from Fig. 1 that it is best to study the composition of the bismuth selenourea complex in the spectrum region 400 to 530 mμ, since all the remaining components of the system being studied, with the exception of the bismuth selenourea complex, only exhibit weak absorption in this region. 0.02 M solutions of selenourea and bismuth nitrate were prepared in order to determine the composition of the complexes. The nitric acid concentration in both solutions was 1 mole/liter. The solutions were mixed in various proportions so that the total volume of the solutions was constant, and the optical density was measured at 405 and 510 mμ. The optical density of the solution at 405 mμ characterizes the formation of the yellow complex, while that at 510 mμ characterizes formation of the red complex. The results of experiments carried out at 405 mμ are represented in Fig. 2, while those at 510 mμ are given in Fig. 3. It is obvious from Fig. 2 that the yellow bismuth selenourea complex is formed at a ratio of bismuth to selenourea of 1:9. Fig. 3 shows that the red bismuth selenourea complex is formed at a bismuth to selenourea ratio of 1:12. The sharp break on the left-hand side of the curve from the maximum (Figs. 2 and 3) indicates that at lower ratios of selenourea and bismuth there are formed weakly colored complexes with a smaller coordination number. The experiments we carried out showed that the red bismuth selenourea complex is only formed at a large excess of selenourea, or at concentrations of the reactants not less then 0.2 mole/liter. At lower concentrations, formation of yellow-colored complexes occurs. In order to explain the nature of the formation of the complexes, absorption curves were also prepared for mixtures of solutions of bismuth nitrate and selenourea. It is evident from Fig. 4 that for ratios of bismuth and selenourea ranging from 1:1 to 1:10, only one maximum appears in the ultraviolet region. At a

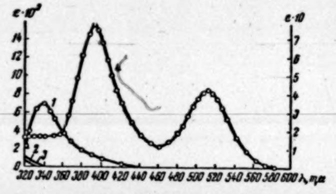

Fig. 1. Light-absorption curves (SF-4 spectrophotometer).

1) Selenourea; 2) nitric acid; 3) bismuth nitrate; 4) bismuth selenourea complexes; at a 3500-fold excess of selenourea, the reference solution contains the same amount of selenourea. The molar extinction coefficient of the bismuth selenourea complex is plotted along the ordinate, starting from the left, while the molar extinction coefficients for all other solutions are plotted on the ordinate starting from the right.

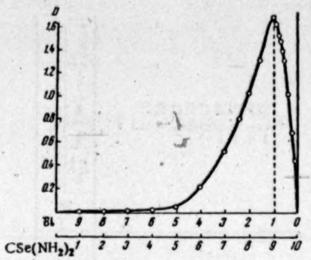

Fig. 2. Composition – light-absorption curve for the yellow bismuth selenourea complex. The ratio of the volumes of 0.02 M solutions of the reactants is plotted along the abscissa.

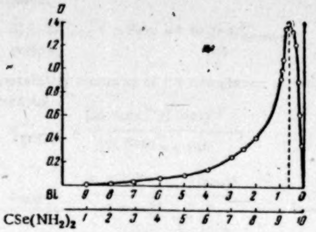

Fig. 3. Composition – light-absorption curve for the red bismuth selenourea complex. The ratio of the volume of 0.02 M solutions of the reactants is plotted along the abscissa.

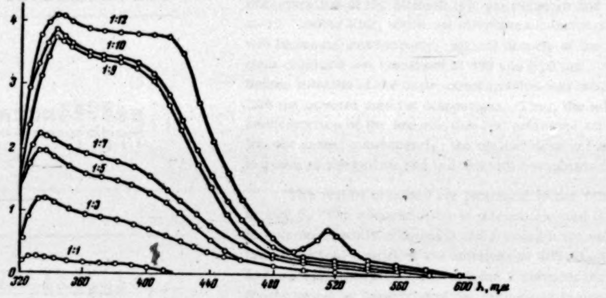

Fig. 4. Light-absorption curves for bismuth selenourea complexes for various ratios of bismuth and selenourea.

ratio of bismuth to selenourea of 1:12, a second maximum appears at 510 mμ. The diffuseness of the maximum in the ultraviolet region can be explained by the formation of bismuth selenourea complexes with a different coordination number, and, in addition, by the presence of free selenourea, which absorbs in the ultraviolet. Free selenourea is present in solution as a result of the dissociation of the bismuth selenourea complexes.

3. A Study of the Stability of Bismuth Selenourea Complexes

The stability of bismuth selenourea complexes is of great importance for characterizing the conditions of their formation, and also for their application in analysis.

Formation of the yellow bismuth selenourea complex can be represented as follows*

$$\underset{\text{colorless}}{\mathrm{Bi\,Sem}_x^{3+}} + n\,\mathrm{Sem} \rightleftharpoons \underset{\text{yellow}}{\mathrm{Bi\,Sem}_{x+m}^{3+}} \qquad (1)$$

---

* Here and henceforth Sem will denote $CSe(NH_2)_2$

C_{Sem}	$-\log C_{Sem}$	D_{405}	$[Bi\,Sem^{3+}_{x+m}]$ mole/liter	$-\log \frac{[Bi\,Sem^{3+}_{x+m}]}{[Bi^{3+}_{tot.}]-[Bi\,Sem^{3+}_{x+m}]}$	D_{510}	$[Bi\,Sem^{3+}_{x+m+n}]$ mole/liter	$-\log \frac{[Bi\,Sem^{3+}_{x+m+n}]}{[Bi^{3+}_{tot.}]-[Bi\,Sem+^{3+}_{x+m+n}]}$
0.0004	3.40	0.062	$0.5\cdot10^{-5}$	1.28	—	—	—
0.0008	3.10	0.085	$0.69\cdot10^{-5}$	1.13	—	—	—
0.0016	2.80	0.241	$1.96\cdot10^{-5}$	0.61	0.005	$0.5\cdot10^{-6}$	2.29
0.004	2.40	0.40	$3.25\cdot10^{-5}$	0.32	0.016	$1.63\cdot10^{-6}$	1.78
0.008	2.10	0.571	$4.74\cdot10^{-5}$	0.054	0.057	$5.8\cdot10^{-6}$	1.21
0.016	1.80	0.720	$5.85\cdot10^{-5}$	−0.146	0.156	$1.88\cdot10^{-5}$	0.73
0.04	1.40	0.886	$7.2\cdot10^{-5}$	−0.410	0.400	$4.06\cdot10^{-5}$	0.17
0.08	1.10	0.980	$7.96\cdot10^{-5}$	−0.590	0.569	$5.77\cdot10^{-5}$	−0.13
0.18	0.75	1.02	$8.3\cdot10^{-5}$	−0.69	0.730	$7.41\cdot10^{-5}$	−0.46
0.36	0.45	1.22	$9.92\cdot10^{-5}$	−1.09	0.942	$9.58\cdot10^{-5}$	−1.36
0.489	0.31	1.24	10^{-4}	—	0.982	$9.98\cdot10^{-5}$	−2.70
0.652	0.19	1.23	10^{-4}	—	0.985	10^{-4}	—

while formation of the red complex can be represented by the scheme:

$$\underset{\text{yellow}}{Bi\,Sem^{3+}_{x+m}} + n\,Sem \rightleftharpoons \underset{\text{red}}{Bi\,Sem^{3+}_{x+m+n}} \qquad (2)$$

The instability constants of the complexes will accordingly be given by

$$K_{yellow} = \frac{[Bi\,Sem^{3+}_{x}]\,[Sem]^m}{[Bi\,Sem^{3+}_{x+m}]} \qquad (3)$$

$$K_{red} = \frac{[Bi\,Sem^{3+}_{x+m}]\,[Sem]^n}{[Bi\,Sem^{3+}_{x+m+n}]} \qquad (4)$$

The extent to which bismuth is complexed as the yellow and red complexes depends on the selenourea concentration.

We used an optical method [4, 5] for determining the numerical values of the instability constants of the yellow and red bismuth selenourea complexes. For this purpose, a series of solutions was prepared in which the concentration of the bismuth salt was constant and equal to 10^{-4} mole/liter, while the selenourea concentration was increased continuously; optical density of the solutions obtained was measured at 405 and 510 mμ. A selenourea solution of the same concentration was introduced into the cuvette used for comparison. Thus, the selenourea concentration of the test solution and reference solution was the same; consequently, the optical density found corresponds to the yellow and red bismuth complexes formed.

The results obtained are presented in the table and in Fig. 5. The concentration of selenourea used is given in column 1, while columns 3 and 6 contain the values for the optical density of the solutions at 405 (D_{405}) and 510 mμ (D_{510}), respectively; column 2 contains the values for the negative logarithm of the selenourea concentration; columns 4 and 7 give the respective concentrations of the yellow and red selenourea complexes; columns 5 and 8 contain the values of the negative logarithm of the ratio of the concentrations of the corresponding complex, and the concentration of the bismuth remaining which has not gone into the corresponding complex.

On the basis of equation (3), the concentration of the yellow bismuth selenourea complex can be expressed as follows:

$$[Bi\,Sem^{3+}_{x+m}] = \frac{[Bi\,Sem^{3+}_{x}]\,[Sem]^m}{K_{yellow\ complex}}$$

Taking logarithms for this equation, we get:

$$\log[Bi\,Sem^{3+}_{x+m}] = \log[Bi\,Sem^{3+}_{x}] + m\log[Sem] - \log K_{yellow\ complex} \qquad (6)$$

When a large excess of selenourea is taken, then on shifting the equilibrium (1) and (2), the selenourea concentration hardly changes at all. Further, the concentration of the colorless complex $[\mathrm{Bi\ Sem}^{3+}_{x}]$ is practically equal to the difference between the total concentration of bismuth $[\mathrm{Bi}^{3+}_{\mathrm{total}}]$ and the concentration of the yellow complex $[\mathrm{Bi\ Sem}^{3+}_{\mathrm{total}}]$.

$$[\mathrm{Bi\ Sem}^{3+}_{x}] = [\mathrm{Bi}^{3+}_{\mathrm{total}}] - [\mathrm{Bi\ Sem}^{3+}_{x+m}] \qquad (7)$$

Substituting this value in equation (6), we get

$$\log[\mathrm{Bi\ Sem}^{3+}_{x+m}] = \log([\mathrm{Bi}^{3+}_{\mathrm{total}}] - [\mathrm{Bi\ Sem}^{3+}_{x+m}]) + m \log[\mathrm{Sem}] - \log K_{\text{yellow complex}}$$

or

$$\log \frac{[\mathrm{Bi\ Sem}^{3+}_{x+m}]}{[\mathrm{Bi}^{3+}_{\mathrm{total}}] - [\mathrm{Bi\ Sem}^{3+}_{x+m}]} - m \log[\mathrm{Sem}] + \log K_{\text{yellow complex}} = 0.$$

By differentiating this equation, we get:

$$\frac{d \log \dfrac{[\mathrm{Bi\ Sem}^{3+}_{x+m}]}{[\mathrm{Bi}^{3+}_{\mathrm{total}}] - [\mathrm{Bi\ Sem}^{3+}_{x+m}]}}{d \log[\mathrm{Sem}]} = m. \qquad (8)$$

Similarly, for the case of formation of the red complex, equation (4) can be transformed into equation (9):

$$\frac{d \log \dfrac{[\mathrm{Bi\ Sem}^{3+}_{x+m+n}]}{[\mathrm{Bi}^{3+}_{\mathrm{total}}] - [\mathrm{Bi\ Sem}^{3+}_{x+m+n}]}}{d \log[\mathrm{Sem}]} = n. \qquad (9)$$

The concentration of the yellow complex is equal to the product of the total (initial) concentration of bismuth (10^{-4} mole/liter) and the ratio $D_{405\,y}/D_{405\,a}$, where $D_{405\,y}$ is the measured value of the optical density at 405 mμ, for a different excess of selenourea, and $D_{405\,a}$ is the optical density of the solution for a selenourea concentration which corresponds to complete complexing of the bismuth as the yellow complex:

$$[\mathrm{Bi\ Sem}^{3+}_{x+m}] = [\mathrm{Bi}^{3+}_{\mathrm{total}}] \frac{D_{405\,y}}{D_{405\,a}}. \qquad (10)$$

In the same way, the concentration of the red complex can be calculated by means of the equation:

$$[\mathrm{Bi\ Sem}^{3+}_{x+m+n}] = [\mathrm{Bi}^{3+}_{\mathrm{total}}] \frac{D_{510\,y}}{D_{510\,a}},$$

where $D_{510\,y}$ is the measured value of the optical density at 510 mμ, for a different excess of selenourea, and $D_{510\,a}$ is the optical density of the solution at a concentration of selenourea which corresponds to practically complete complexing of the bismuth as the red complex.

Equations (8) and (9) correspond to the equation for a straight line. When the values of the negative logarithms of the selenourea concentration and the respective ratios of the concentration of the complex to the concentration of free metal ions are plotted on the same scale on a graph, the slope of the straight line in the case of the yellow complex will have the value m, while the slope of the straight line in the case of the red complex will be equal to n.

The tabulated results are plotted graphically in Fig. 6 for the yellow complex, and in Fig. 7 for the red complex.

Curves 1, 2, and 3 in Figs. 6 and 7 correspond to values for m and n of 1, 2, and 3, while the points denote the values obtained experimentally. As can be seen from Fig. 6, the selenourea concentration affects formation of the yellow complex to the first degree. According to Fig. 7 it is evident that the square of the concentration affects formation of the red selenourea complex.

Taking into account all that has been said above, and also the composition — optical density curves (Figs. 2 and 3), the equations for the formation of colored bismuth selenourea complexes, obviously, can be depicted as follows:

$$\underset{\text{weakly colored}}{BiSem_8^{3+}} + Sem \rightleftharpoons \underset{\text{yellow}}{BiSem_9^{3+}}. \tag{12}$$

$$\underset{\text{yellow}}{BiSem_9^{3+}} + Sem \rightleftharpoons \underset{\text{yellow}}{BiSem_{10}^{3+}} \tag{13}$$

$$\underset{\text{yellow}}{BiSem_{10}^{3+}} + 2Sem \rightleftharpoons \underset{\text{red}}{BiSem_{12}^{3+}} \tag{14}$$

from which

$$K_{\text{yellow complex}} = \frac{[BiSem_8^{3+}][Sem]}{[BiSem_9^{3+}]} \tag{15}$$

$$K_{\text{red complex}} = \frac{[BiSem_{10}^{3+}][Sem]^2}{[BiSem_{12}^{3+}]}. \tag{16}$$

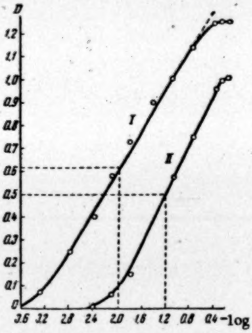

Fig. 5. Relation between optical density of solutions of bismuth selenourea complexes and selenourea concentration: I) yellow complex at 405 mμ; II) red complex at 510 mμ.

It is clear from equation (15) that when half of the bismuth has been bound as the yellow complex, the numerical value of the instability constant of the yellow complex is equal to the concentration of excess selenourea. Equation (16) shows that when half of the bismuth has been bound as the red complex, the numerical value of the instability constant of the red complex is equal to the square of the concentration of excess selenourea. The concentration of excess selenourea is readily found from the curves in Fig. 5. When half of the bismuth has been bound as the yellow complex, the optical density of the solution at 405 mμ will be equal to half the optical density of a solution in which the bismuth is almost completely bound as in the yellow complex. From Curve 1 in Fig. 5, it is clear that the optical density of the solution at this point will be equal to 1.22/2 = 0.61. This value of the optical density on Curve 1 corresponds to a concentration of excess bismuth of 10 moles/liter, while the approximate numerical value of the instability constant of the yellow complex will obviously be equal to:

$$K_{\text{yellow complex}} = \frac{[BiSem_8^{3+}][Sem]}{[BiSem_9^{3+}]} = 10^{-2}.$$

From the curve in Fig. 5, similarly, we can find the concentration of excess selenourea when half the bismuth has been bound as the red complex. This concentration is equal to $10^{-1.2}$ mole/liter, while the approximate value of the instability constant of the red complex will be equal to:

$$K_{\text{red complex}} = \frac{[BiSem_{10}^{3+}][Sem]^2}{[BiSem_{12}^{3+}]} = (10^{-1.25})^2 = 10^{-2.5}.$$

The value of the instability constant of the yellow bismuth complex shows that the bismuth selenourea complex is more stable than the corresponding thiourea complex, the numerical value of whose instability constant is equal to 6.4×10^{-2} [6].

It follows from this that selenourea forms comparatively stable and intensely colored complexes with bismuth, which can be used for the qualitative detection and for the photometric determination of bismuth. The sensitivity of the reaction for bismuth is 2.5 μg Bi/ml for the red complex, and 1 μg Bi/ml for the yellow complex.

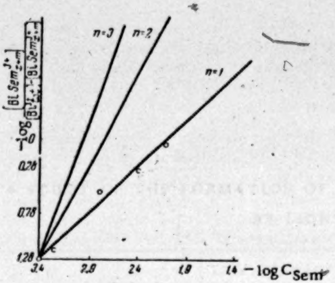

Fig. 6. Effect of excess selenourea on the formation of the yellow bismuth selenourea complex .

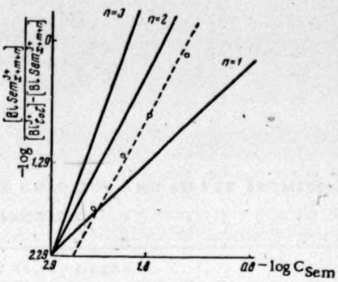

Fig. 7. Effect of excess selenourea on the formation of the red bismuth selenourea complex .

SUMMARY

A study has been made of the qualitative reactions of heavy-metal cations with selenourea: in the course of this study it has been found that bismuth, antimony, tin, arsenic, gold, and palladium give color reactions with selenourea. Characteristic insoluble compounds are formed by lead ions, and also, at high concentrations, by ions of trivalent iron; copper, divalent mercury, and silver form colorless complexes which readily dissolve in water. These complexes are highly stable.

The composition and stability of bismuth selenourea complexes have been investigated. It has been shown that bismuth forms two colored complexes in solution: a yellow complex at a ratio of bismuth to selenourea of 1:9, and a red complex at a ratio of bismuth to selenourea of 1:12.

The stability of the bismuth selenourea complexes are characterized by the following approximate values for their instability constants:

$$K_{\text{yellow complex}} = \frac{[BiSem^{3+}_{8}][Sem]}{[BiSem^{3+}_{9}]} = 10^{-2}$$

$$K_{\text{red complex}} = \frac{[BiSem^{3+}_{10}][Sem]^{2}}{[BiSem^{3+}_{12}]} = 10^{-2.5}$$

The sensitivity of the reaction for bismuth with selenourea based on formation of the red complex is 2.5 μg Bi/ml, while the sensitivity is 1 μg Bi/ml when formation of the yellow complex is used as a basis.

The sensitivity of the reaction for bismuth using selenourea as reagent is higher than when thiourea is used.

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A STUDY OF THE FORMATION OF SILVER CHLORIDE AND SILVER BROMIDE BY LIGHT EXTINCTION

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In a previous article [1] we published results of a study of various systems containing silver iodide, by the light-extinction method. It was shown then that there is a relation between the solubility of AgI suspensions and their light-extinction. The present article contains results of a similar study carried out with silver chloride and silver bromide.

The Systems $AgNo_3 - KBr - H_2O$ and $AgNo_3 - KCl - H_2O$

(Determination of the Composition of the Precipitates)

These systems were studied by the method of isomolar series. The sum of the molar concentrations of $AgNO_3$ and the potassium halide (KBr, KCl) amounted to 8×10^{-3} mole/liter. In contrast to the system $AgNO_3 - KI - H_2O$ [1], in the present instance gelatin was used for stabilizing the degree of dispersion of the precipitates of AgBr and AgCl, which changes rapidly with time, with consequent changes in light extinction. The amount of gelatin was 0.02 % in all mixtures.

TABLE 1

Extinction in the System $AgNO_3 - KBr - H_2O$

($\Sigma_{AgNO_3 + KBr} = 8 \times 10^{-3}$ mole/liter)

№	$\frac{KBr}{AgNO_3}$	Extinction	Molar extinction coefficient
1	0.07	0	0
2	0.33	0.11	20.8
3	0.5	0.18	25.4
4	0.8	0.39	41.5
5	1.0	0.42	39.6
6	1.25	0.30	31.8
7	2	0.18	25.4
8	3	0.13	24.5
9	10	0.06	31.0
10	15	0.01	7.5

TABLE 2

Extinction in the System $AgNO_3 - KCl - H_2O$

($\Sigma_{AgNO_3 + KCl} = 8 \times 10^{-3}$ mole/liter)

№	$\frac{KCl}{AgNO_3}$	Extinction	Molar extinction coefficient
1	0.1	0.06	31
2	0.33	0.21	38
3	0.5	0.27	39
4	0.8	0.36	38
5	1	0.64	60
6	1.25	0.47	50
7	2	0.27	38
8	3	0.16	30
9	10	0.06	31

As can be seen from the measurements for the light extinction in mixtures, which are given in Tables 1 and 2, and depicted in Figs. 1 and 2, the light-extinction maximum of the suspensions is found on the composition ordinate at points corresponding to a ratio of $AgNO_3 : KX$ equal to 1 (X = Br, Cl). Worthy of attention is the fact that the curves on both sides of the maximum are arranged practically symmetrically, and intersect each other at an acute angle. It is obvious that for the concentrations used, the degree of dispersion of the precipitates changes to practically the same extent on both sides of the equivalence point.

The results obtained once again testify to the possibility of determining the composition of a precipitate by the light-extinction method, even when the degree of dispersion of the precipitate is not constant as a result of the predominating effect on the light extinction of the amount of the mass of precipitate. Naturally, the variability of the degree of dispersion should not exceed the limits of certain values.

The Systems $AgBr-KBr-H_2O$ and $AgCl-KCl-H_2O$

The systems $AgBr - KBr - H_2O$ and $AgCl - KCl - H_2O$ were studied from the same point of view as the system $AgI - KI - H_2O$, with the aim of establishing the effect which might be shown by Br^- and Cl^- ions on the light extinction of AgBr and AgCl suspensions, since these ions are known to exhibit a dissolving action(at the appropriate concentrations) with respect to silver bromide and silver chloride. The $AgNO_3$ concentration was constant in all experiments, and was equal to 10^{-3} mole/ liter, while the concentrations of KBr and KCl were changed, in the case of mixtures with AgCl from 10^{-2} to 1.2 mole/ liter, and for mixtures with AgCl from 10^{-3} to 2.4 mole/ liter.

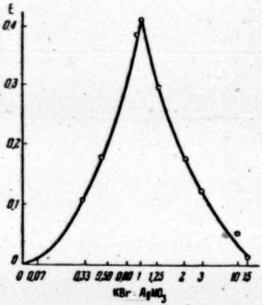

Fig. 1. Extinction in the system
$AgNO_3 - KBr - H_2O$.
$\Sigma_{AgNO_3 + KBr} = 8 \times 10^{-3}$ mole/ liter.

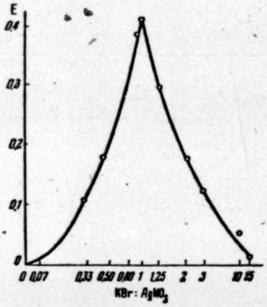

Fig. 2. Extinction in the system
$AgNO_3 - KCl - H_2O$.
$\Sigma_{AgNO_3 + KCl} = 8 \times 10^{-3}$ mole/ liter.

As can be seen from the results of measurements of the light extinction of the mixtures,which are given in Tables 3 and 4, and in Figs. 3 and 4, increasing the concentration of Br^- and Cl^- ions up to a certain point leads to an increase in extinction, this increase, as in the case of the system $AgI - KI - H_2O$ which we studied, being

TABLE 3

Extinction in the System
$AgBr - KBr - H_2O$
(constant concentration of
$AgBr = 1 \times 10^{-3}$ mole/ liter)

No.	[KCl] excess in mol/1.	-log[KCl] excess	Extinction	Molar extinction coefficient
1	$1 \cdot 10^{-3}$	3	0.03	11
2	$1 \cdot 10^{-2}$	2	0.03	11
3	$7.5 \cdot 10^{-2}$	1.1	0.15	56
4	$1 \cdot 10^{-1}$	1	0.38	143
5	$2 \cdot 10^{-1}$	0.7	0.38	143
6	1.0	0	0.33	124
7	1.6	−0.2	0.31	117
8	2.0	−0.3	0.19	71
9	2.4	−0.38	0	0

TABLE 4

Extinction in the System
$AgCl - KCl - H_2O$
(constant concentration of
$AgCl = 1 \times 10^{-3}$ mole/ liter)

No.	[KBr] excess mol/1.	-log[KBr] excess	Extinction	Molar extinction coefficient
1	$1 \cdot 10^{-2}$	2	0.01	3.76
2	$2.5 \cdot 10^{-2}$	1.6	0.01	3.76
3	$5 \cdot 10^{-2}$	1.3	0.03	11.30
4	$7.5 \cdot 10^{-2}$	1.12	0.05	18.80
5	$1 \cdot 10^{-1}$	1	0.64	242.00
6	$2 \cdot 10^{-1}$	0.7	0.62	234.00
7	$5 \cdot 10^{-1}$	0.3	0.53	200.00
8	1.2	−0.08	0.10	37.60
9	1.5	−0.18	0	0

the result of an increase in the solubility of the suspension. On comparing the results obtained for the systems $AgBr - KBr - H_2O$ and $AgCl-KCl-H_2O$, with the results for the corresponding system with AgI, a striking feature is the almost identical shape of the curves. The maximum value of the extinction, in all three cases, is located in the region bordering on the values for excess potassium halide concentration, namely within the limits 10^{-1} to 2×10^{-1} mole/liter.

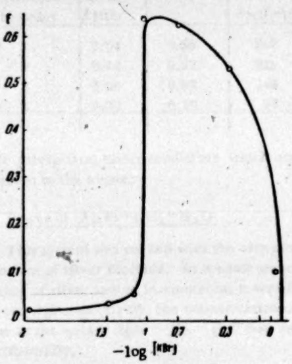

Fig. 3. Extinction in the system $AgBr-KBr-H_2O$. $[AgBr] = 1 \times 10^{-3}$ mole/liter.

The relation which exists between the solubility of AgCl and the extinction of its suspensions, is confirmed by the diagram for the solubility of AgCl in NaCl solution which we adduce; this diagram is based on results obtained by Berne and Leden [2] who used radioactive silver Ag^{110} for their work. As is evident from Fig. 5, the solubility of AgCl, at NaCl concentrations ranging from 10^{-3} to 10^{-2} mole/liter does not change significantly. At higher NaCl concentrations, the solubility of silver choride increases sharply; in accordance with this, extinction in suspensions of AgCl increases also. Obviously, the coarsening of AgCl suspensions, which is necessary for attaining a maximum value for the extinction, occurs in each individual case at a definite value for its solubility. Further increases in the solubility of the suspension lead to such an increase in particle size that its exinction passes through a maximum. It is essential to point out that the strong increase in extinction by suspensions of AgCl occurs precisely in that concentration range of NaCl where there is a strong increase in its solubility (from 10^{-2} to 2×10^{-1} mole NaCl / liter).

By comparing the values of the molar extinction coefficient at the maximum for the system under discussion (at 0.1 and 0.2 mole/liter), one can see that, despite a certain decrease in the amount of solid phase (AgCl), in the second case, the value of the absorption remains practically the same. Consequently, the decrease in the amount of solid phase, in this case, is compensated by the excess in the increase of extinction as a result of coarsening of the particles. This is also observable for extinction values at concentrations of 1 mole/liter of KCl. According to the results of the authors quoted above, the solubility of AgCl at NaCl concentrations of 1 mole/liter, is equal to 0.2×10^{-3} mole/liter; consequently, 80 % of the original amount of AgCl in the system remains in the solid phase. Nevertheless, the molar extinction coefficient decreases to 87 % of its maximum value (124 instead of 143). Thus, even for this value of the solubility of AgCl, the coarsening of the particles of the precipitate continues to predominate over the effect of the

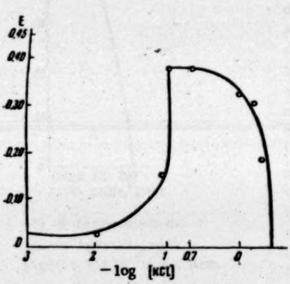

Fig. 4. Extinction in the system $AgCl-KCl-H_2O$. $[AgCl] = 1 \times 10^{-3}$ mole/liter.

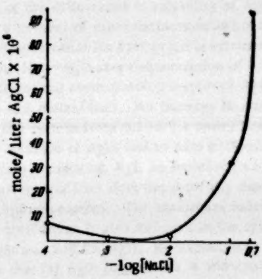

Fig. 5. Solubility of AgCl in NaCl solutions.

dissolving of the precipitate (or, at least, still compensates for a decrease in extinction as the result of the dissolving of the AgCl). Naturally, when even more AgCl dissolves, the decrease in the amount of solid phase must, in the final count, result in a drop in extinction right down to zero value.

From what has been said, it becomes evident that the view advanced by I. V. Tananaev regarding the nature of the change in extinction in accordance with the solubility of the solid phase (coarsening and dissolving of the precipitate), is confirmed in the given actual system AgCl–KCl–H_2O. Unfortunately, there is only a small number of instances of studies of the solubility of very sparingly soluble precipitates under conditions which could be taken into account when the question is considered in a similar fashion to the above.

TABLE 5

Extinction in the System AgBr–NH_3–H_2O (AgBr concentration = 1×10^{-3} mole/liter)

No. of experiment in order	NH_3, in mole/liter	Extinction	Molar extinction coefficient
1	0.04	0.55	208
2	0.10	0.57	215
3	0.20	0.39	148
4	0.30	0.10	37

The System AgBr–NH_3–H_2O

This system was studied with the aim of establishing the effect of NH_3 as a solvent on light extinction by suspensions of silver bromide. As a consequence of the greater solubility of silver bromide in ammonia as compared with that of silver iodide in ammonia, it would be natural to assume that for an equal content of the solid-phase AgBr and AgI respectively, the concentration of ammonia necessary for attaining maximum light extinction will be less in the system AgBr – NH_3 – H_2O than in the corresponding system AgI – NH_3 – H_2O. This was confirmed experimentally.

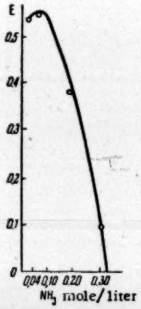

Fig. 6. Extinction in the system AgBr–NH_3–H_2O. [AgBr] = 1×10^{-3} mole/liter.

We measured extinction in mixtures containing equivalent amounts of $AgNO_3$ and KBr of 10^{-3} mole/liter, and consequently 10^{-3} mole/liter of AgBr, and varying amounts of ammonia.

From the results given in Table 5 and in Fig. 6, it is evident that in the given system there occurs a sharp increase in extinction by the suspensions on addition of ammonia. In addition, as the result of the differences in solubility of AgBr and AgI in ammonia, a number of other characteristics are observed, namely: the maximum value for extinction is attained for AgBr in the system AgBr–NH_3–H_2O at a concentration of 0.1 mole/liter of ammonia, while for the corresponding system of AgI, the ammonia concentration is 2 moles/liter. An increase in ammonia concentration in the test system from 0.1 to 0.4 mole/liter leads, in fact, to complete solution of AgBr and to zero extinction. In the corresponding system containing AgI, an increase in ammonia content from 2 to 4 moles/liter does not show any essential effect on extinction by AgI suspensions. The maximum value of the molar extinction coefficient is also different in the systems indicated (215 for AgBr and 248 for AgI). No explanation can be found for the fact that for AgBr suspensions, a maximum value of the molar extinction coefficient, in contrast to AgI suspensions, is achieved in the system AgBr–KBr–H_2O and not in the system AgBr–NH_3–H_2O.

The System AgBr–$AgNO_3$–NH_3–H_2O

This system was studied, like the corresponding system with AgI, in order to establish the nature of the effect of excess Ag^+ ions in the presence of ammonia on extinction by AgBr suspensions.

We carried out two series of experiments. In the first series the concentration of excess silver nitrate was 4×10^{-3} mole/liter, while in the second series it was 9×10^{-3} mole/liter. The remaining conditions were the same as those used in the previous system AgI – NH_3 – H_2O. As can be seen from the results given in Table 6 and

7, and on Figs. 7 and 8, the nature of the light extinction curves for AgBr suspensions remains the same as in the case where there is no excess $AgNO_3$. Extinction in both cases increases with increasing NH_3 concentration, passes through a maximum and then decreases to zero. As one would expect, the region occupied by the maximum expands significantly in the presence of $AgNO_3$, and is more significant the greater the excess of silver nitrate. In accordance with this, the point at which practically the whole of the precipitate dissolves is shifted to the right in the region of the higher ammonia concentration; in the first instance (for an excess of $AgNO_3$) it is shifted from 4×10^{-3} to 0.7 mole/liter, while in the second case (for an excess of $AgNO_3$ from 9×10^{-3} to 1 mole/liter).

TABLE 6

Extinction in the System
$AgBr-AgNO_3-NH_3-H_2O$
(AgBr concentration = 1×10^{-3} mole/liter;
$AgNO_{3(excess)}$ concentration =
= 4×10^{-3} mole/liter).

Number	NH_3, in mole/liter	Extinction	Molar extinction coefficient
1	0.04	0.55	207
2	0.10	0.59	222
3	0.20	0.60	226
4	0.30	0.55	207
5	0.50	0.38	143
6	0.70	0.03	11

TABLE 7

Extinction in the System
$AgBr-AgNO_3-NH_3-H_2O$
(AgBr concentration = 1×10^{-3} mole/liter;
$AgNO_{3\,(excess)}$ concentration =
= 9×10^{-3} mole/liter).

Number	NH_3, in mole/liter	Extinction	Molar extinction coefficient
1	0.04	0.53	200
2	0.10	0.57	215
3	0.30	0.58	219
4	0.50	0.52	196
5	0.70	0.35	124
6	1.00	0.02	7

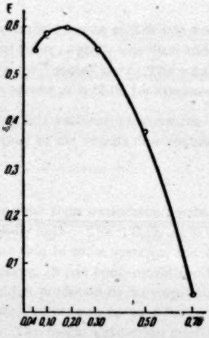

Fig. 7. Extinction in the system
$AgBr-AgNO_3-NH_3-H_2O$.
$[AgBr] = 1 \times 10^{-3}$ mole/liter;
$[AgNO_3]_{excess} = 4 \times 10^{-3}$ mole/liter.

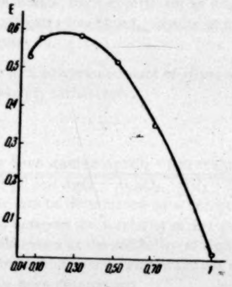

Fig. 8. Extinction in the system
$AgBr-AgNO_3-NH_3-H_2O$.
$[AgBr] = 1 \times 10^{-3}$ mole/liter;
$[AgNO_3]_{excess} = 9 \times 10^{-3}$ mole/liter.

On comparing the results obtained during a study of the systems $AgI-AgNO_3-NH_3-H_2O$ and $AgBr-AgNO_3-H_2O$, in which the concentrations of the solid phase and excess silver nitrate were the same ($C_{AgBr} = C_{AgI} = 10^{-3}$ mole/liter, $C_{AgNO_3\,(excess)} = 4 \times 10^{-3}$ mole/liter), it is clear that there is sharp difference in the effect of ammonia on extinction by suspensions of AgBr and AgI; while extinction of AgBr is practically zero at an NH_3 concentration of 0.7 mole/liter, extinction by AgI becomes a maximum only at 2 mole/liter, and practically remains unchanged even on increasing the ammonia concentration to 4 moles/liter. This fact indicates that it should be possible to carry out phototurbidimetric determination of iodides in the presence of bromides. As an example of the practical use of a such a possibility we measured extinction in mixtures containing 10^{-3} mole/liter of silver bromide and iodide, 4 mole/liter of ammonia and 4×10^{-3} mole/liter $AgNO_3$. The extinction by this mixture proved to be 0.58, i.e. almost the same as for the same amount of silver iodide in the absence of silver bromide.

Phototurbidimetric Determination of Silver by Means of a Calibration Curve

In preparing the system $AgBr-KBr-H_2O$, we found that in the presence of excess KBr in a concentration of approximately 0.1 mole/liter, there was a sharp increase in extinction by AgBr suspensions. Taking into account these conditions, we made an attempt to carry out a phototurbidimetric determination of silver by means of a calibration curve.

TABLE 8

Phototurbidimetric Determination of Silver

Ag^+, in gram ions/liter		Error, in %
Taken	Found	
$2 \cdot 10^{-4}$	$1.97 \cdot 10^{-4}$	−1.5
$4 \cdot 10^{-4}$	$4.07 \cdot 10^{-4}$	+1.8
$6 \cdot 10^{-4}$	$6.17 \cdot 10^{-4}$	+2.8
$8 \cdot 10^{-4}$	$8.4 \cdot 10^{-4}$	+5.0

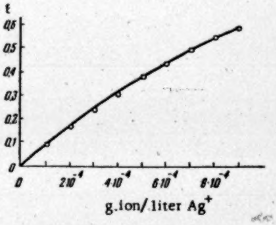

Fig. 9. Calibration curve for phototurbidimetric determination of silver by means of KBr.

The same amount of KBr was added to the cell each time so that its concentration in the final volume was 10^{-1} mole/liter; $AgNO_3$ was then added, with stirring, in varying amounts from experiment to experiment, of 10^{-4} to 9×10^{-4} mole/liter. The total volume of the mixtures in all cases was 50 ml. Results of extinction measurements served as a basis for construction of a calibration curve (Fig. 9).

Using this calibration curve the content of silver in solutions with unknown amount of silver was determined. The accuracy of the results thus obtained (Table 8) proved completely satisfactory.

SUMMARY

Using the light extinction method the following systems have been studied $AgNO_3 - KBr - H_2O$; $AgNO_3 - KCl - H_2O$, $AgBr - KBr - H_2O$; $AgBr - NH_3 - H_2O$, $AgCl - KCl - H_2O$ and $AgBr - AgNO_3 - NH_3 + H_2O$. It has been shown that in these systems, the composition of the precipitate can be determined on a composition–property diagram. It has been established that there is a close relation between the solubility of the precipitate and the extinction produced by its suspensions. It has been shown that increases in the solubility of AgBr suspensions to a certain extent, can be used for increasing the sensitivity of phototurbidimetric determinations of silver considerably. The molar extinction coefficients of AgBr and AgCl have been determined.

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* Original Russian pagination. See C. B. Translation.

DIALKYL- AND DIARYLDITHIOPHOSPHORIC ACIDS AS ANALYTICAL REAGENTS

COMMUNICATION 3. DETERMINATION OF PALLADIUM BY MEANS OF NICKEL OR POTASSIUM DIALKYL AND DIARYLDITHIOPHOSPHATES*

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Palladium ions form sparingly soluble compounds with dialkyl- and diaryldithiophosphates [1]. Although these reagents precipitate other elements of the platinum group, nevertheless, by creating certain conditions and using complexing agents, it is possible to determine palladium readily by means of diethylphosphoric acid in the presence of platinum, iridium, and also in the presence of a number of base elements.

To date a considerable number of methods have been published for the gravimetric, titrimetric, and photometric determinations of palladium. Palladium has been determined gravimetrically by means of dimethylglyoxime [2-6], methylbenzoylglyoxime [6], salicylaldoxime[6, 7], α-benzoinoxime [7], β-furfuraldoxime [7, 8], α-furildioxime [7, 9], 1,2-cyclohexanedionedioxime [10], 4-methyl- and 4-iospropyl 1,2-cyclohexanedionedioxime [11], 3-hydroxy-1,3-diphenylhydrazine [12], 1-hydroxy-diphenyltriazine [12], violuric acid [13], 1,2,3-benzotriazole [14], phenylthiourea, thiophenol, and thiobarbituric acid [15], and substituted aniline acids [16]. Palladium has been precipitated and weighed as palladium bis-ethylenediamine tetraiodomercuriate [17], as the sulfide [18], and in other forms. Palladium has been determined by an indirect complexometric method [19-22], by titration with potassium iodide [23, 24], and with other reagents [25 - 28]. Palladium has been determined photometrically by means of iodide [29 - 31], bromide [32], thiocyanate [33, 34], methylglyoxime [5, 35, 36], dimethylglyoxime [5, 35-37], salicylaldoxime [35, 36], β-hydroxynaphthaldoxime [36], β-furfurylaldoxime [38], α-furildioxime [32], nitrosonaphthol [39], reagents containing the p-nitrosophenylamino group [40, 41, 42], thiourea [43], 2-mercapto-4,5-dimethylthiazole [44], disodium ethylenediaminetetracetate [45], and by formation of palladium purpurate [46], etc. A critical discussion of photometric methods of determining palladium can be found in the article by Beamish and McBryde [47]. Information on other methods for the quantitative determination of palladium is to be found in a number of reviews [48 - 51].

Most of the methods of determining palladium have not found wide use in practice because they are not selective enough, or the organic reagents are not readily available, or because of the complexity of the techniques involved. The most frequently used method is precipitation with dimethylglyoxime. When, however, platinum is present (the element which accompanies palladium most often), this simple and accurate method can only yield accurate results by strict adherence to the specified conditions. It is pointed out in Gillebrand and Lendel's book [52] that dimethylglyoxime partially precipitates platinum if the solution is heated. Many of the methods of determining palladium presuppose preliminary separation of palladium from platinum and other elements, and this of course means complications.

On mixing solutions of palladium chloride with nickel dimethyl- or diethyldithiophosphate, there is formed a yellow-orange, finely crystalline precipitate, which is insoluble, even in concentrated strong acids (hydrochloric, sulfuric). The precipitate can be readily filtered and centrifuged. Washing of the precipitate is not accompanied by peptization. The precipitate is readily soluble in organic solvents (chloroform, carbon tetrachloride, diethyl ether) forming yellow-orange solutions. The sensitivity of detection of palladium with a 0.005 N solution of nickel diethyldithiophosphate in weakly acid media is 1:500,000, while in strongly acid media (0.1 N HCl) it is 1:1,000,000. The limit of identification is 1 γ of Pd.

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* For No. 1 see J. Anal. Chem. 11, 523 (1956) and for No. 2 see Bull. Moscow State University, No. 2, 177 (1957).

Palladium dimethyl- and diethyldithiophosphates are negligibly soluble. After precipitation of palladium, the latter cannot be detected in the centrifugate either by potassium iodide or dimethylglyoxime. Thus, palladium is precipitated quantitatively by the dithiophosphates. It is interesting to note that palladium dimethylglyoximate, in the form of an aqueous suspension (pH 3-4) slowly changes into palladium diethyldithiophosphate on adding nickel diethyldithiophosphate at room temperature. The same occurs in the case of palladium iodide, and the soluble iodide complex of palladium, which is regarded as one of the most stable compounds of palladium. However, dialkyl- and diaryldithiophosphoric acids do not precipitate palladium from alkaline solutions containing excess cyanides.

Palladium diethyldithiophosphate which has been well washed with water and dried in air to constant weight has a sharp melting point at 119°. Recrystallization from acetone does not affect the melting point, indicating the purity of the compound obtained.

It is demonstrated in the present article that it is possible to use dialkyl- and diaryldithiophosphoric acids for solving problems in the analytical chemistry of palladium.

A Study of the Reaction between Palladium Ions and Dialkyl- and Diaryldithiophosphates and the Properties of the Palladium Compounds Formed

Palladium solutions were prepared by dissolving its chloride in 0.1 N HCl.

Two solutions which were standardized by means of the dimethylglyoxime method were found to contain 0.00283 and 0.00276 g Pd/ml. More dilute solutions of palladium chloride were prepared by diluting the original solutions (in 0.1 N HCl) with water, and, in some cases, with 0.1 N HCl.

The dithiophosphoric acids (dimethyl-, diethyl-, diisobutyl-, diphenyl- and dibenzyldithiophosphoric acids) were used as the nickel salts. Doubly recrystallized nickel diethyldithiophosphate has a melting point of 105-106°. Diethyldithiophosphoric acid was also used as its potassium salt. The solutions were standardized by addition of standard iodine, and excess of the latter titrated with thiosulfate.

Chloroform and carbon tetrachloride were purified by the usual methods. All the other reagents used (potassium iodide, sodium bisulfite, etc.) were analytical grade materials or chemically pure grade materials, and were not purified further.

Photometric measurements in the ultraviolet and in the visible were carried out on the SF-4 spectrophotometer using a hydrogen lamp or a filament lamp. The layer thickness in the quartz cell was always 10.01 mm. The setup for amperometric titration with a rotating platinum electrode was assembled as usual.

Quantitative Study of the Reaction between Palladium Ions and Diethyldithiophosphate

a) Visual Titration. On addition of an aqueous solution of $[(C_2H_5O)_2PSS]_2Ni$ to an intensely red colored solution of the iodide complex of palladium, the latter is decolorized and a yellow precipitate is formed. The reaction proceeds quantitatively and practically instantaneously in the cold. The reaction end point is fixed fairly definitely by a change in color produced by addition of one drop of reagent solution.

Palladium chloride solutions were titrated as follows. To a known volume of standard palladium solution was added crystalline potassium iodide until the precipitate of palladium iodide which originally separated out, had dissolved, and an intensely colored, transparent solution was formed. The solution prepared in this way was titrated from a tapless microburet with a solution of $[(C_2H_5O)_2PSS]_2Ni$ until the red-brown color of precipitate and solution had changed to yellow on addition of one drop of titrant. The results obtained are given in Table 1. The end point (color change) during titration was observed at a molar ratio of $PdCl_2 : [(C_2H_5O)_2PSS]_2Ni = 1 : 1$.

b) Amperometric Titration. Dialkyldithiophosphate anions are oxidized on the dropping mercury electrode and on the rotating platinum micro anode [53]. The half-wave potential $E_{1/2}$ relative to the saturated calomel electrode is +0.697 volt in the case of the platinum micro electrode (a 10^{-3} M solution of sodium diethyldithiophosphate in 0.1000 M perchloric acid was electrolyzed). A linear relation is observed between the concentration of dithiophosphate ions and the diffusion current.

TABLE 1

Determination of Molar Ratios During Interaction of $PdCl_2$ with $[(C_2H_5O)_2PSS]_2Ni$ by Visual Titration

Amount $PdCl_2$ soln. taken T_{Pd} – 0.00283		Used amount of $[(C_2H_5O)_2PSS]_2Ni$ M – 0.0245		Ratio $\frac{M_{PdCl_2}}{M_{[(C_2H_5O)_2PSS]_2Ni}}$
in ml	mmoles	in ml	mmoles	
0.50	0.0132	0.54	0.0132	1.00
0.75	0.0198	0.82	0.0201	0.99
1.00	0.0264	1.10	0.0269	0.98
1.50	0.0396	1.63	0.0400	0.99
2.00	0.0528	2.18	0.0535	0.99

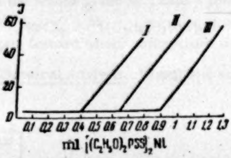

Fig. 1. Amperometric titration of palladium ions with nickel diethyldithiophosphate in a supporting electrolyte of 0.1 N HCl: I) 1 ml $PdCl_2$; II) 1.5 ml $PdCl_2$; III) 2 ml $PdCl_2$.

Palladium diethyldithiophosphate was titrated amperometrically with a rotating platinum micro anode at a a potential of +0.8 volt relative to the saturated calomel electrode in a supporting electrolyte 0.1 N HCl. Divalent palladium ions are not oxidized at this potential to the quadrivalent state. The titration curve is of the usual form (Fig. 1).

The intersection point of the two branches of the curve obtained by amperometric titration (Table 2) corresponds to a molar ratio of $PdCl_2 : [(C_2H_5O)_2PSS]_2Ni = 1 : 1$.

c) Spectrophotometric Method. Standard solutions of palladium chloride and nickel diethyldithiophosphate were mixed in known proportions, the compounds formed were then extracted with three lots of carbon tetrachloride of 10, 5, and 5 ml respectively. The combined extracts in the next separating funnel were washed with an equal volume of water or 1 M NaOH to remove any possible excess of nickel diethyldithiophosphate or diethyldithiophosphoric acid, which interfere with photometric determination of the palladium complex. It was established in special experiments that one washing with NaOH solution serves to transfer the nickel diethyldithiophsophate practically completely into the aqueous phase, while all the palladium diethyldithiophosphate remains in the organic phase. The washed extract was filtered through a dry filter paper, and the filtrate diluted in a standard 25 ml flask to the mark with the organic solvent. The optical

TABLE 2

Determination of the Molar Ratios during Interaction of $PdCl_2$ with $[(C_2H_5O)_2PSS]_2Ni$ by Amperometric Titration

Solution taken of $PdCl_2$, T_{Pd} – 0.00283		Used amount of $[(C_2H_5O)_2PSS]_2Ni$ M – 0.0256		Ratio $\frac{M_{PdCl_2}}{M_{[(C_2H_5O)_2PSS]_2Ni}}$
In ml	mmoles	in ml	mmoles	
0.50	0.0132	0.51	0.0131	1.01
0.75	0.0198	0.77	0.0197	1.00
1.00	0.0264	1.00	0.0256	1.03

density of the extract was measured on a spectrophotometer at 295 mμ (maximum absorption for palladium diethyldithiophosphate occurs at this wave length).

TABLE 3

Spectrophotometric Determinationof the Composition of Palladium Diethyldithiophosphate

PdCl$_2$ solution taken T_{Pd} – 0.000283		Used amount of $[(C_2H_5O)_2PSS]_2Ni$ T_{NiR_2} – 0.000210		Ratio $\frac{M_{PdCl_2}}{M_{[(C_2H_5O)_2PSS]_2Ni}}$	Optical density
in ml	in millimols	in ml	in millimols		
3.00	0.000795	0.50	0.000252	3.15	0.175
3.00	0.000795	1.00	0.000504	1.58	0.527
3.00	0.000795	1.50	0.000756	1.05	0 850
3.00	0.000795	2.00	0.001008	0.785	0.920
2.80	0.000743	2.00	0.001008	0.735	0.860
2.20	0.000582	2.00	0.001008	0.578	0.675
1.20	0.000340	2.00	0.001008	0.337	0.430

From the results given in Table 3 and reproduced on Fig. 2, it is clear that maximum absorption corresponds to a ratio of M_{PdCl_2} : $M_{[(C_2H_5O)_2PSS]_2Ni}$ which approximates to unity. Thus, under the conditions used, a compound is again formed whose composition corresponds to the formula $[(C_2H_5O)_2PSS]_2Pd$.

d) Chemical Analysis. Visual and amperometric titration, as well as spectrophotometric methods, demonstrated that palladium chloride and diethyldithiophosphate interact at a molar ratio of 1 : 1. Nevertheless, these methods do not solve the question of the content of palladium in the palladium compound formed, which may contain water of crystallization. Consequently, palladium was determined gravimetrically in the precipitate. (Table 4). The filtered and well-washed precipitate obtained by adding excess of nickel diethyldithiophosphate to a solution of palladium chloride was dried in air to constant weight. Purity was controlled by means of its melting point of 119°. An aliquot of the precipitate prepared in this way was oxidized with aqua regia on heating. After removal of most of the acid by evaporation, water was added to the residue, and the solution made weakly acid. Palladium was then precipitated as the dimethylgyoximate which was weighed after the necessary treatment.

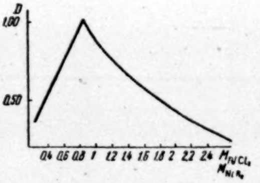

Fig. 2. Spectrophotometric determination of the composition of palladium diethyldithiophosphate.

The mean of three determinations (22.9 %) corresponds, within the limits of experimental error, with the calculated content (22.4 %) based on the fomula $[(C_2H_5O)_2PSS]_2Pd$.

TABLE 4

Determination of Palladium in the Precipitate by a Micro Gravimetric Method

Weight of palladium diethyldithiophosphate	Weight of palladium dimethylglyoximate	Weight of palladium	Palladium content of the diethyldithiophosphate
0.01635	0.01210	0.00383	23.4
0.03610	0.02635	0.00835	23.2
0.02833	0.02007	0.00622	22.0
		Mean	22.9 %

The agreement between the calculated and experimental values for the palladium content indicates that the precipitate which has been dried in air does not contain water of crystallization, and has the fomula $[(C_2H_5O)_2PSS]_2Pd$.

Thus, these various methods show that palladium chloride reacts with nickel diethyldithiophosphate as follows:

$$PdCl_2 + [(C_2H_5O)_2PSS]_2Ni = [(C_2H_5O)_2PSS]_2Pd + NiCl_2$$

There is no reason for assuming that other soluble dialkyl- and diaryldithiophosphates will react otherwise with palladium ions.

The constancy of the composition of the precipitate obtained under different conditions, as well as the quantitative precipitation of palladium, permit one to develop titrimetric, gravimetric, and photometric methods for its determination.

Microgravimetric Determination of Palladium

Palladium diethyldithiophosphate satisfied the requirements for precipitation and weighing. Palladium can also be weighed as the dimethyldithiophosphate, although the conversion factor to palladium in this case is somewhat smaller than in the case of the diethyldithiophosphate. Palladium diisobutyl-, diphenyl-, and dibenzyldithiophosphates cannot be recommended as gravimetric forms, since they melt below 100° (e.g., palladium dibenzyldithiophosphate melts at 70°), and this complicates drying. Drying in a vacuum desiccator at room temperature takes longer than drying at 105°.

Palladium can be precipitated by nickel diethyldithiophosphate and other water soluble dithiophosphates, in the presence of platinum, copper, iron, and other elements which usually accompany palladium, as long as the solution contains an appropriate complexing agent.

In order to keep platinum in solution during gravimetric (and also titrimetric) determination of palladium, sodium bisulfite is added. When this is done quadrivalent platinum is reduced to the divalent state, and a stable, colorless complex is formed, probably $Na_6[Pt(SO_3)_4]$ [54]. Bisulfite has already been used for masking platinum during the photometric determination of rhodium [54], and for the photometric determination of copper during analysis of platinum – copper alloys [55]. It has been found [55] that complete decolorization of a solution of quadrivalent platinum is achieve at pH 5; at pH 3 the yellow color of platinum disappears slowly. Our experiments showed that the sulfite complex of divalent platinum is formed only on addition of excess sodium bisulfite to a weakly acid solution. Nevertheless, the sulfite complex formed is stable during subsequent addition of significant amounts of hydrochloric acid (even at a concentration of 1 N HCl).

Iron, copper, and lead can be kept in solution by addition of Complexone III and adjusting the pH to about 9.

To 0.5 - 2 ml of solution of palladium chloride containing 0.00138 - 0.00283 g of palladium, was added a 1.5 - 2 fold excess of 0.025 M solution of nickel diethyldithiophosphate. The precipitate deposited was allowed to stand for one hour in contact with the mother liquor and then filtered through a porcelain micro crucible; after quantitatively transferring the precipitate to the crucible, it was washed three times with water, and then dried to constant weight at 105° in a drying oven and weighed on a micro balance. During determination of palladium in the presence of platinum, excess of sodium bisulfite was added to the solution prior to precipitation of the palladium. During determination of palladium in the presence of iron, copper, and lead, interference from these elements was prevented by addition of 0.5 g of Complexone III (Trilon B) and 1.5 g of sodium-potassium tartrate, and the pH adjusted to about 9 with ammonia. In the presence of iron, copper, lead, and platinum, bisulfite was also added to the solution as well as Complexone III before precipitation of palladium. The precipitate was kept for one hour on a water bath and then filtered.

The results given in Table 5 show that there is no interference with determination of palladium in the presence of amounts of platinum, copper, iron, and lead which are greater than that of the palladium. Further, nickel, cobalt, aluminum, zinc, chromium, and a few other elements do not interfere with palladium determination either. The method gives accurate and readily reproducible results.

TABLE 5

Determination of Palladium by Means of Nickel Diethyldithiophosphate (conversion factor to palladium 0.2236)

Pd taken as solution, in g	Weight of precipitate $[(C_2H_5O)_2PSS]_2Pd$ in g	Pd found, in g	Amounts of other elements added, in g	Error	
				Absolute, in g	Relative in %
0.00283	0.01342	0.00296	—	+0.00013	+4.3
0.00142	0.00642	0.00144	—	+0.00002	+1.4
0.00142	0.00640	0.00143	—	+0.00001	+0.7
0.00283	0.01285	0.00287	0.005 Pt	+0.00003	+1.1
0.00276	0.01246	0.00279	0.005 Pt	+0.00003	+1.1
0.00138	0.00607	0.00136	0.025 Pt	−0.00002	−1.4
0.00138	0.00611	0.00136	0.025 Pt	−0.00002	−1.4
0.00138	0.00599	0.00134	0.05 Pt	−0.00004	−2.8
0.00276	0.01259	0.00281	0.03 Cu ($CuSO_4$)	+0.00005	+1.8
0.00276	0.01242	0.00277	0.1 Pb ($Pb(NO_3)_2$)	+0.00001	+0.4
0.00276	0.01245	0.00278	0.02 Fe ($FeCl_3$)	+0.00002	+0.7
0.00276	0.01311	0.00293	0.03 Cu + 0.1Pb + + 0.02 Fe	+0.00017	+6
0.00226	0.01263	0.00282	0.03 Cu + 0.1 Pb + +0.02 Fe	+0.00006	+2
0.00276	0.01248	0.00290	0.03 Cu + 0.1 Pb + + 0.02 Fe	+0.00013	+5
0.00276	0.01242	0.00278	0.03 Cu + 0.1 Pb + + 0.02 Fe + 0.02Pt	+0.00002	+0.7
0.00276	0.01240	0.00277	0.03 Cu + 0.1 Pb+0.02 Fe + 0.02 Pt	−0.00001	−0.4
0.00276	0.01274	0.00284	0.03 Cu + 0.1 Pb + +0.02 Fe	+0.00008	+2.9

Determination of Palladium by Visual Titration
(In the presence of platinum)

In addition to the fact that the reaction between the intensely colored iodide complex of palladium and nickel diethyldithiophosphate at room temperature is very rapid, and that the reaction follows a strictly defined equation, it is also accompanied by a fairly good color change at the end point. As a result of systematic experiments, the following technique has been developed for the visual titration of palladium in the presence of platinum.

To 1-2 ml of a solution of palladium chloride containing 1.5-4.5 mg (and up to 15) of palladium, was added potassium iodide in such amount that its concentration was about 0.5 g/ml, an equal volume of 2 M hydrochloric acid was then added, and the transparent cherry-red colored solution titrated with nickel diethyldithiophosphate from a microburet, until the brown color of the solution disappeared, and a precipitate with a yellow color appeared, part of the latter being suspended in the liquid. For determination of palladium in the presence of platinum, after addition of potassium iodide to the weakly acid test solution, a 10-20 fold excess of sodium bisulfite was added. When this was done, the solution acquired a weak yellow color as a result of the breakdown of the palladium iodide complex and the formation of a stable sulfite complex of divalent platinum. The solution was then acidified with hydrochloric acid until it acquired an intense color from the palladium iodide complex formed; under these conditions the sulfite complex of divalent platinum remained unchanged. The solution prepared in this way was titrated with nickel diethyldithiophosphate solution,as indicated above.

The visual method of titrating palladium gives accurate results (Table 6). The error is, apparently, mainly the result of errors in measuring the volumes of the solutions. The method may find practical application during analysis of platinum—palladium alloys. When the alloys contain copper as well, the method is inapplicable.

Thiourea, as well as sodium nitrite (after removal of excess of it with urea), is not suitable for complexing platinum during titrimetric determination of palladium.

Photometric Determination of Palladium

As pointed out already, the isolated and washed precipitates of palladium dialkyl- and diaryldithiophosphates readily dissolve in chloroform, carbon tetrachloride, and other organic solvents. The precipitates also dissolve readily in those cases where they are found in the form of suspensions in acid solutions. In weakly alkaline solutions containing complexing agents, palladium dithiophosphates are only extracted slowly.

TABLE 6

Determination of Palladium by Visual Titration in the Presence of Platinum

$PdCl_2$ taken (2.84 mg/ml Pd) in ml	Pt added as 0.1 M H_2PtCl_2 in mg	Amount of $[(C_2H_5O)_2PSS]_2$ Ni used, in ml	Pd taken in mg	Pd found in mg	Error	
					Absolute, in mg	Relative, in %
0.50	—	0.53	1.42	1.38	−0.04	−2.8
0.50	—	0.55	1.42	1.44	+0.02	+1.4
1.00	—	1.10	2.84	2.87	+0.03	+1
1.50	—	1.58	4.26	4.13	−0.13	−3
1.50	—	1.60	4.26	4.17	−0.09	−2.1
2.0	—	2.20	5.68	5.76	+0.12	+2.1
0.50	5	0.59	1.42	1.38	−0.04	−2.8
0.50	15	0.54	1.42	1.41	−0.01	−0.7
1.00	5	1.09	2.84	2.85	−0.01	−0.35
1.00	10	1.10	2.84	2.88	+0.04	+1.4
1.50	10	1.58	4.26	4.13	−0.13	−3

The extracts obtained have a yellow-orange color when the palladium concentration is greater than 0.4 mg Pd in 25 ml of carbon tetrachloride. At lower palladium concentrations (e.g., at a content of 0.083 mg Pd in 25 ml of carbon tetrachloride) the extracts are completely colorless. The absorption curves for palladium diethyldithiophosphate in carbon tetrachloride are shown on Fig. 3. For comparison, absorption curves for solutions of nickel diethyldithiophosphate, diethyldithiophosphoric acid, and disulfide are given on the same diagram. Similar curves were obtained for solutions in chloroform.

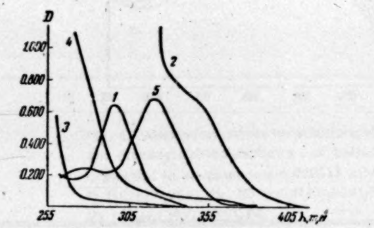

Fig. 3. Absorption curves for palladium diethyldithiophosphate, nickel diethyldithiophosphate, diethyldithiophosphoric acid, and the disulfide. 1) 0.0545 mg of palladium diethyldithiophosphate in 25 ml CCl_4 (a solution which is colorless to the eye); 2) 0.83 mg palladium diethyldithiophosphate in 25 ml CCl_4 (solution yellow to the eye); 3) 20 mg of diethyldithiosphosphoric acid in 25 ml CCl_4; 4) 2.6 mg of disulfide in 25 ml CCl_4; 5) 0.4 mg in 25 ml CCl_4.

The absorption curves were taken as follows. To a palladium chloride solution in 0.1 N HCl, containing 0.0545 or 0.83 mg Pd, was added 1.0 ml of 0.035 M potassium diethyldithiophosphate, and the palladium diethyldithiophosphate formed extracted three times with 5-ml lots of carbon tetrachloride. The extracts were filtered through a dry filter paper, the filtrates were collected in a 25 ml standard flask, and diluted to the mark with carbon tetrachloride.

When the absorption curves for palladium compounds were taken on an SF-4 spectrophotometer with a hydrogen lamp and with a filament lamp, a quartz cell was used with a layer thickness of 10.01 mm for the liquid. The solvent was used as the blank.

The nickel diethyldithiophosphate solution (0.4 mg in 25 ml of carbon tetrachloride) was prepared by appropriate dilution of a solution of 50 mg $[(C_2H_5O)_2PSS]_2Ni$ (exact weight) in 25 ml of carbon tetrachloride.

The diethyldithiophosphoric acid solution was obtained by mixing 1.0 ml of 0.05 M potassium diethyldithiophosphate and 1.0 ml of 1 M HCl in a separating funnel, and the freed diethyldithiophosphoric acid extracted with carbon tetrachloride (three lots of 5.0 ml); the extracts were filtered through a dry filter paper, and the filtrates diluted in a 25.0 ml standard flask to the mark with carbon tetrachloride.

Special experiments showed that diethyldithiophosphoric acid and palladium diethyldithiophosphate are practically quantitatively extracted, under the experimental conditions employed, by the first lot of carbon tetrachloride.

The absorption maximum for palladium diethyldithiophosphate is found in the ultraviolet at 295 mμ, while the absorption maximum for nickel diethyldithiophosphate is located at 320 mμ. Diethyldithiophosphoric acid appreciably absorbs at wave lengths less than 275 mμ. It may get into the palladium diethyldithiophosphate solution during its preparation, nevertheless, it has practically no effect on the absorption of the solution. The solution of nickel diethyldithiophosphate absorbs appreciably at 295 mμ. Consequently, in order to get accurate results during the photometric determination of palladium at 295 mμ, using nickel diethyldithiophosphate which is readily obtained in pure form, it is necessary to remove excess of the latter by some method. Tests have shown that nickel diethyldithiophosphate can be readily washed out from the extract by a double washing with distilled water or by one washing with 0.1 M sodium hydroxide or sodium bicarbonate *; under these condition, all the palladium diethyldithiophosphate remains in the organic phase (even on washing twice with 1 M sodium hydroxide).

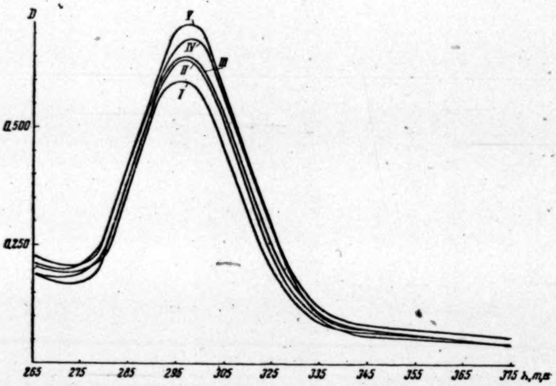

Fig. 4. Absorption curves for solutions of the dimethyl-, diisobutyl-, diphenyl-, and dibenzyldithiophosphates of palladium in carbon tetrachloride. The concentration in all cases was 0.000518 mM of the dithiophosphate in 25 ml CCl_4. I) $[(CH_3O)_2PSS]_2Pd$; II) $[(C_2H_5O)_2PSS]_2Pd$; III) $[(C_4H_9O)_2PSS]_2Pd$; IV) $[(C_6H_5O)_2PSS]_2Pd$; V) $[(C_6H_5CH_2O)_2PSS]_2Pd$.

The absorption curves of palladium diemthyl-, diethyl-, diisobutyl-, diphenyl-, and dibenzyldithiophosphates in carbon tetrachloride are shown in Fig. 4.

Solutions for spectrophotomeric measurements were prepared as follows. To 2.00 ml of palladium chloride solution (T_{Pd} = 0.00276) in 0.001 N HCl, contained in a separating funnel, was added 5 ml of a solution of nickel dialkyl- or diaryldithiophosphate (2 mg/ ml) in carbon tetrachloride, the mixture was thoroughly agitated and then 1 M sodium hydroxide solution added. After the phases had separated out, the carbon tetrachloride solution was colorless. The solution was next acidified by addition of 5 ml of sulfuric acid 1 : 1, another 5 ml of carbon tetrachloride was added and the palladium dithiophosphate extracted. The extraction was repeated three times. In order to remove excess reagent, the extract was vigorously shaken with 10 ml of 1 M sodium hydroxide. The washed extract was transferred to a 25 ml standard flask. The alkali solution was washed once again with carbon tetrachloride. After dilution to the mark absorption curves were taken. All the solutions contained 0.000518 millimole of dithiophosphate in 25 ml carbon tetrachloride.

The absorption maxima of the solutions of all the palladium dialkyl- and diaryldithiophosphates in carbon tetrachloride studied differ insignificantly from each other.

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* For washing, there is no need to add tartrate to the solution in the case of such small amounts of nickel diethyldithiophosphate as are usually found in the extract.

The molar extinction coefficients at 295 mμ are as follows:

$$[(CH_3O)_2PSS]_2Pd - 2.85 \cdot 10^4; \quad [(C_2H_5O)_2PSS]_2Pd - 3.1 \cdot 10^4; \quad [(C_4H_9O)_2PSS]_2Pd - 3.15 \cdot 10^4;$$
$$[(C_6H_5O)_2PSS]_2Pd - 3.35 \cdot 10^4; \quad [(C_6H_5CH_2O)_2PSS]_2Pd - 3.45 \cdot 10^4.$$

Differences in the values lie almost within the limits of reproducibility of spectrophotometric measurements.

To a first approximation it may be considered that all the diaryl- and dialkyldithiophosphates studied possess almost equal sensitivity with respect to palladium. Taking into account the high solubility of nickel diethyldithiophosphate, and its ready availability compared with the diisobutyl-, diphenyl-, and dibenzyldithiosphosphates of nickel, it is more expedient to use nickel diethyldithiophosphate for photometric determination of palladium, although satisfactory results can be obtained by means of the other dithiophosphates. The potassium or sodium salt of diethyldithiophosphoric acid can also be used.

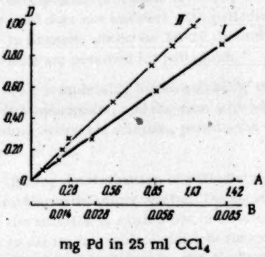

Fig. 5. Compliance with Beer's law of solutions of palladium diethyldithiophosphate in CCl$_4$ at 295 mμ (Curve I) and at 340 mμ (Curve II)

Palladium can be determined photometrically at 295 mμ (maximum absorption) and also visually on the basis of the intensity of the yellow color. Solutions of palladium diethyldithiophosphate conform to Beer's law at 295 mμ (Fig. 5) within the limits of 0.014 to 0.090 mg Pd in 25 ml carbon tetrachloride (optical density from 0.160 to 0.90). Yellow solutions of palladium diethyldithiophosphate can be measured colorimetrically (visually) or can be measured on a spectrophotometer at 340 mμ. In this case the solutions conform with Beer's law within the limits 0.16 to 1.1 mg of Pd in 25 ml of carbon tetrachloride (optical density 0.15 to 0.90).

During photometric determination of palladium, 1-2 ml of 0.005 N nickel diethyldithiophosphate was added to a solution containing 0.015-0.10 mg of palladium, the mixture was acidified with an equal volume of 2 M hydrochloric acid or 50% acetic acid, and the palladium extracted in succession with 10, 5, and 5 ml of carbon tetrachloride. The extracts were collected in a separating funnel and washed with an equal volume of water or 1 M sodium hydroxide to remove excess reagent. The organic phase was collected after passage through a filter in a 25 ml standard flask, it was diluted to the mark with carbon tetrachloride and the optical density measured at 295 mμ.

The amount of palladium was found from the calibration curve.

When platinum was present, about 0.1 g of sodium bisulfite was added to the test solution, and dissolved by shaking. The precipitate which separated out was dissolved by addition of 1 M hydrochloric acid, and diluted with the same volume of hydrochloric acid of equal concentration. Determination of palladium was completed as described above.

In acid and neutral solutions, cupric ions oxidized diethyldithiophosphate to disulfide [1]. The disulfide is extracted with organic solvents at the same time as cuprous diethyldithiophsophate, and interferes with palladium determination. Interference from the dithiosphosphates of divalent and univalent copper can readily be suppressed by washing them out of the extracts in carbon tetrachloride with alkali solution. We have not succeeded in finding a method of removing disulfide from the extract. Consequently, when carrying out determinations, it is essential to avoid formation of disulfide, by reducing copper to the univalent state by means of sodium sulfide (about 0.5 g per ml of solution). To the colorless solution obtained was therefore added excess nickel diethyldithiophosphate with respect to the expected amount of palladium and copper; this was followed by addition of an equal volume of 1 M hydrochloric acid, the palladium was extracted, and the extracts collected in a separating funnel and washed once with an equal volume of 1 M sodium hydroxide. Palladium determination was then completed as described above. When platinum is also present as well as copper, it does not interfere with palladium determination; trivalent gold does not interfere either, since it is reduced to the metal by sulfite.

Determination of palladium in the presence of lead is of great practical importance. On dissolving lead beads in nitric acid, palladium dissolves along with lead; the other platinum metals do not dissolve. The method developed by Frazer, Beamish, and McBryde [31] for the determination of palladium in the presence of lead is extremely complicated and involves many operations. It is possible by using nickel diethyldithiophosphate to determine palladium rapidly and reliably in the presence of large amounts of lead. The method is based on the fact that palladium forms a less soluble diethyldithiophosphate than lead, and on the fact that lead diethyldithiophosphate is readily removed from the extract in carbon tetrachloride by washing with sodium hydroxide solution. To the test solution containing traces of palladium and large amounts of lead was added an excess of nickel diethyldithiophosphate with respect to the palladium; the solution was slightly acidified with nitric acid and the palladium extracted with carbon tetrachloride. The subsequent procedure was the same as that described above.

Antimony diethyldithiophosphate absorbs in the ultraviolet and in the visible part of the spectrum adjacent to the ultraviolet, and, consequently, interferes with the direct determination of palladium. All the same, antimony diethyldithiophsophate is readily washed out of the extract in carbon tetrachloride by sodium hydroxide solution, and does not interfere with palladium determination. Determination is possible in the presence of antimony in amounts which are 10-20 times that of the palladium. In the presence of very large amounts of antimony, low results are obtained for palladium.

The considerably higher solubility of iron diethyldithiophsophate as compared with that of palladium diethyldithiophsophate, and the ease with which it can be washed out of the extract in carbon tetrachloride by means of sodium hydroxide solution, permits the successful determination of palladium in the presence of considerable amounts of iron.

During determination of palladium in the presence of large amounts of copper and iron, we did not succeed in obtaining satisfactory results. During reduction of copper with sulfite, trivalent iron is not completely reduced, since the reaction is carried out in an alkaline medium. During the subsequent acidification of the solution in order to create favorable conditions for extraction of palladium diethyldithiophosphate, univalent copper, apparently, is oxidized by trivalent iron, the divalent copper formed oxidizes the diethyldithiophosphate to disulfide, and this interferes with palladium determination. Determination of palladium is possible at a ratio of Pd : Cu : Fe = 1:1:1 as long as the copper concentration does not exceed 0.0001 M. Palladium can be determined by the standard series method. It was pointed out above that at comparatively high concentrations of palladium diethyldithiophosphate, the organic solvents are colored yellow-orange. Since the solutions conform to Beer's law, within certain limits, the palladium can be determined by visual photometric measurements. A series of solutions of palladium diethyldithiophosphate containing 0.279, 0.32, 0.36, 0.425, 0.455, 0.56, 0.615 mg of Pd in 5 ml of carbon tetrachloride were prepared as follows: a known volume of a standard palladium chloride solution was placed in a test tube used for colorimetric measurements, and 0.5 ml of 0.05 M nickel diethyldithiophosphate added, followed by an equal volume of 1 M HCl (the volume of the aqueous pahse was 5 ml), and 5 ml of carbon tetrachloride. The test tube was then vigorously shaken, and the aqueous layer poured off as completely as possible, 3-5 ml of 1 M sodium hydroxide solution was added to the test tube and the whole again shaken. Washing with alkali solution was carried out to remove excess nickel diethyldithiophosphate from the organic phase, as well as for removal of other elements. During determination of palladium in the presence of other elements (platinum, iron, antimony, lead, nickel) the procedure was the same as for the preparation of standard series. Copper should be reduced beforehand by addition of sodium sulfite (0.5 g per ml of test solution).

Tables 7 and 8 contain some of the results obtained during photometric determination of palladium.

SUMMARY

1. Dialkyl- and diaryldithiophosphates quantitatively precipitate palladium from acid, neutral, and also alkali solutions containing complexing maerials. During a study of the reaction between palladium iodide and diethyldithiophosphoric acid by various methods, it was established that it proceeds under various conditions in accordance with the equation:

$$PdCl_2 + [(C_2H_5O)_2PSS]_2Ni = [(C_2H_5O)_2PSS]_2Pd + NiCl_2$$

2. Palladium diethyl- as well as dimethyldithiophosphate answer all the requirements in yielding a precipitate which is suitable for gravimetric purposes. A microgravimetric method has been developed for determination of palladium in the presence of platinum, nickel, iron, copper, and other elements. The method gives

sufficiently accurate and reproducible results.

TABLE 7

Photometric Determination of Palladium (at 295 mμ) in the Presence of Other Elements

Pd taken, in mg	Metal added, in mg	Ratio Pd : Me	Pd found, in mg	Error	
				Absolute, in mg	Relative, in %
0.0568	—	—	0.0560	—0.0008	—1.4
0.0810	—	—	0.0820	+0.0010	+1.2
0.0142	—	—	0.0145	+0.0003	+2
0.0142	5 Pt	1 : 350	0.0140	—0.0002	—1.4
0.0142	10 Pt	1 : 700	0.0146	+0.0004	+2.7
0.0284	2.5 Pt	1 : 90	0.0286	+0.0002	+0.7
0.0568	2.5 Pt	1 : 45	0.0557	—0.0011	—2
0.0852	5 Pt	1 : 120	0.0870	+0.0018	+2
0.0852	5 Pt	1 : 120	0.08664	+0.0012	1.4
0.0142	30 Pt	1 : 2000	0.0139	0.0003	—2
0.0568	1.25 Cu	1 : 20	0.0550	—0.0014	—3
0.0284	2.5 Cu	1 : 80	0.0288	+0.0004	+1.4
0.0142	15 Cu	1 : 1000	0.0142	0	0
0.0568	5 Rh	1 : 90	0.0572	+0.0004	+0.7
0.0284	5 Rh	1 : 180	0.0280	—0.0004	—1.4
0.0284	6 Fe	1 : 210	0.0286	+0.0002	+0.7
0.0142	6 Fe	1 : 420	0.0137	—0.0005	—3.5
0.0284	25 Pb	1 : 880	0.0286	+0.0002	+0.7
0.0142	50 Pb	1 : 3500	0.0142	0	0
0.0284	50 Au	1 : 350	0.0300	+0.0016	+6
0.0284	10 Au	1 : 700	0.0290	+0.0006	+2
0.0284	0.25 Sb	1 : 8	0.0284	0	0
0.0284	0.5 Sb	1 : 16	0.0280	—0.0004	—1.4
0.0284	5Pt + 2.5 Cu	1 : 265	0.0274	—0.0010	—3.5
0.0142	25Pt + 1.5Cu	1 : 265	0.0135	—0.0007	—4.2
0.0276	0.2Fe+0.06Cu	1 : 12	0.0271	—0.0004	—1.5

TABLE 8

Determination of Palladium in the Presence of Other Elements by the Standard Series Method

Pd taken, in mg	Metal added in mg	Ratio Pd : Me	Pd found, in mg	Absolute error, in mg
0.36	12 Pt	1 : 30	0.36	0
0.32	5 Cu	1 : 16	0.32	0
0.56	5 Cu	1 : 8	0.56	0
0.56	10 Sb	1 : 18	0.56	0
0.536	5 Fe	1 : 9	0.536	0
0.279	20 Pb	1 : 72	0.279	0

3. The rapid reaction which occurs between the intensely colored iodide complex of palladium and diethyldithiophosphate at room temperature, and which follows a strictly defined equation is accompanied by a fairly sharp change in color at the equivalence point. The micro method for the titrimetric determination of palladium which is based on this principle, is applicable in the presence of amounts of platinum and other elements which are considerably greater than that of palladium.

4. Solutions of palladium dialkyl- and diaryldithiophosphates in chloroform, carbon tetrachloride, and other organic solvents are yellow-orange in color. A solution of palladium diethyldithiophosphate in carbon tetrachloride exhibits maximum absorption at 295 mμ, and practically coincides with the absorption maxima of palladium dimethyl-, diisobutyl-, diphenyl-, and dibenzyldithiophosphate. The height of the maxima for all the dithiophosphates is of the same order of magnitude. Palladium diethyldithiophosphates conform with Beer's law at 295 mμ within the limits 0.014 mg to 0.090 mg Pd in 25 ml carbon tetrachloride (optical density from 0.16 to 0.90). During photometric determination of palladium the optical density is measured at 295 mμ. Yellow, more concentrated solutions of palladium diethyldithiophosphate, can be colorimetrically determined visually, or can be measured

on a spectrophotometer at 340 mμ. In this case the solution conform with Beer's law within the limits 0.16 to 1.1 mg Pd in 25 ml carbon tetrachloride (optical density 0.15 to 0.90 respectively). The photometric methods which have been developed permit palladium to be determined with reasonable accuracy in the presence of platinum, nickel, copper, iron, gold, lead, antimony, and other elements.

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NEW COMPLEXONES

COMMUNICATION 3. BENZYLAMINEDIACETIC ACID AND α, α', α"-TRIAMINEDIBENZYLDIPHENYLMETHANEHEXAACETIC ACID

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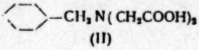
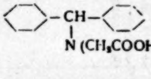
We have made an attempt to study the effect of changes in molecular weight on the complexing properties of certain complexones, taking as examples methylamine diacetic (I), benzylaminediacetic (II), and benzhydrylaminediacetic acids (III).

$CH_3N(CH_2COOH)_2$ (I)



(II)



(III)

The properties of the new compounds were studied by means of the polarographic method, by determining the shift in the half wave potentials of a number of cations.* Results of studies of the complexing properties of benzylaminediacetic acid at various pH's of the solutions are given in Table 1.

It follows from the results given in Table 1 that benzylaminediacetic acid forms complex compounds with Cu^{2+}, Bi^{3+}, Ni^{2+}, Sb^{3+} at pH 2.5; with Cu^{2+}, Co^{2+}, Mo^{V} at pH 4.4; with Pb^{2+}, La^{III} at pH 9.35; and with Cu^{2+}, La^{III}, and Sb^{3+} at pH 12.4.

Results of the polarographic study of disodium benzhydrylaminediacetic acid have been published previously [1].

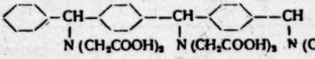
During the study of the effect of changes in molecular weight of the complexones on the stability of the complex compounds formed, a comparison was made of the half wave potentials of the cations of certain heavy metals in the presence of methylamine-, benzylamine-, and benzhydrylaminediacetic acids at pH's of 2.5 and 9.35 (Table 2).

A comparison of the behavior of the acids indicated showed that an increase in the weight of the molecule, under certain conditions, led to an increase in complexing properties.

Thus, in the case of lead at pH 9.35, in the presence of methylaminediacetic acid, the half wave potential is shifted through 0.34 volt, and in the presence of benzylaminediacetic acid the shift is 0.38 volt, while in the presence of benzhydrylaminediacetic acid the complex formed is so stable that the reduction wave for lead disappears.

Polarographic Study of α, α', α"-Triaminedibenzyldiphenylmethanehexaacetic Acid

A study of the shift in half wave potential of α, α', α"-triaminedibenzyldiphenylmethanehexaacetic acid (IV)



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[*] The polarographic study was carried out under conditions similar to those described during an investigation of hexamethylenediaminetetracetic acid, etc. [1].

TABLE 1

Half-Wave Potentials of Cations in the Presence of Benzylaminediacetic Acid and $\alpha, \alpha', \alpha''$-Triaminedibenzyldiphenylmethanehexaacetic Acid (Relative to the Saturated Calomel Electrode)

Cations	pH 2.5			pH 4.4			pH 9.35				pH 12.4		
	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α''-triaminedibenzyldiphenylmethane hexaacetic acid	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α''-triamidedibenzyldiphenylmethane hexaacetic acid	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α''-triaminedibenzyldiphenylmethane hexaacetic acid		$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α''-triaminedibenzyldiphenylmethane hexaacetic acid
									After preparation	After standing for 5 days			
Pb^{2+}	−0.38	−0.38	−0.48 −0.60	−0.43	−0.44	−0.43	−0.18	−0.56	−0.62	−0.62 (−0.58 −1.14)	−0.70	−0.70	−0.65 (−0.62 −1.06 −1.5)
Cu^{2+}	+0.02	−0.12	−0.1 −0.4	−0.02	−0.12	−0.10	−0.29 −0.54	−0.32 (−0.26 −0.76)	−0.23	−0.23	−0.05	−0.46	Disappears
Bi^{3+}	−0.12	−0.28	−0.21	−0.21	−0.28 (−0.66)	−0.18	—	—	—	— (−0.23 −1.04)	0.70	−0.70	−0.66
Cd^{2+}	−0.60	−0.60	−0.60	−0.62	−0.62 (−0.66)	−0.62	−0.62	−0.66	−0.76	−0.78 −1.12 (−0.76)	—	−0,72	—
As^{III}	−1.02	−1.02	Disappears	—	—	—	—	—	−1.72	—	—	(−0,22)	—
Sb^{3+}	−0.19	Disappears	—	−0.38	—	—	—	—	—	—	−1.17	Disappears	—
Sn^{2+}	—	—	—	—	—	—	—	—	—	(−1.20)	—	—	—
Zn^{2+}	−1.08	−1.06	Not reproduced	−1.09	−1.09	−0.94 −(1.08)	−1.28	Not reproduced (−1.38)	−1.10 −1.00	−1.21	−1.47	−1.45	−1.4 (−1.52)
Ni^{2+}	−1.02	−1.1	Disappears	−1.12	−1.12	−1.06	−1.01	−1.01	−1.24	−1.12	−1.37	−1.37	Disappears

TABLE 1 (Continued)

Cations	pH 2.5			pH 4.4			pH 9.35				pH 12.4		
	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylamine-diacetic acid	$E_{1/2}$ in the presence of α,α',α"-triaminedibenzyldiphenylmethane hexaacetic acid	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylamine-diacetic acid	$E_{1/2}$ in the presence of α,α',α"-triaminedibenzyldiphenylmethane hexaacetic acid	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylamine-diacetic acid	$E_{1/2}$ in the presence of α,α',α"-triaminedibenzyldiphenylmethane hexaacetic acid		$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylamine-diacetic acid	$E_{1/2}$ in the presence of α,α',α"-triamidedibenzyldiphenylmethane hexaacetic acid
									After preparation	After standing for 5 days			
CO^{2+}	−1.22	—	Disappears	−1.15	— (−0.64)	−1.21	−1.21	−1.40	−1.26	−1.26	−1.37	—	Disappears
Mn^{2+}	—	−1.35	—	−1.50	—	—	−1.56	−1.64	−1.20 −1.56	−1.20 −1.56	—	(−1.12)	—
Fe^{3+}	—	—	—	—	—	—	—	—	—	—	—	−1.46	—
Cr^{3+}	—	—	—	—	—	—	−1.56	Disappears	—	−1.72 (−1.18)	—	(−0.92)	—
MO^{VI}	−0.52	−0.12 −0.46	— −(0.37)	−0.24 −0.64	−0.58 −1.3	−0.50	—	—	—	—	—	−0.52 −1.2	−1.30 (−1.50,
Ti^{IV}	−0.65 −0.97	—	Precipitate	Precipitate	—	Precipitate	—	(−1.08)	Precipitate	Precipitate (−1.18)	—	—	Precipitate
Al^{3+}	—	—	—	—	— (−0.62)	—	—	—	−1.10	−1.10	−1.21	−1.6 Precipitate	Disappears
Be^{2+}	—	—	—	—	—	—	—	—	−1.11	—	—	—	(−0.88)
La^{III}	−0.62	−0.62	−0.61	−0.72	−0.72	−0.62	−0.68	−0.76	−0.78	—	—	−0.67 −1.26)	

Notes. The values given in brackets are those obtained for $E_{1/2}$ after standing for 5 days in the presence of benzylaminediacetic acid, and after 15 days standing in the presence of α, α', α"-triaminedibenzyldiphenylmethanehexaacetic acid, in those cases where $E_{1/2}$ changes on standing.

showed that this compound forms complexes with Pb^{2+}, Cu^{2+}, As^{III}, Ni^{2+}, Co^{2+}, Mo^{VI} at pH 2.5; with Co^{2+}, Mo^{VI}, and Fe^{3+} at pH 4.4; with Pb^{2+}, Bi^{3+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, Cr^{3+}, and La^{III} at pH 9.35; and with Cu^{2+}, Ni^{2+}, and Al^{3+} at pH 12.4.

TABLE 2

Relation Between Half Wave Potentials and the Stability of the Complexonates Formed

Cations	$E_{1/2}$ without complexone at pH 9.35	$E_{1/2}$ without complexone at pH 2.5	$E_{1/2}$ in the presence of methylaminediacetic acid	$E_{1/2}$ in the presence of methylaminediacetic acid	$E_{1/2}$ in the presence of benzhydrylaminediacetic acid, disodium salt
Cu^{2+}	−0.29−0.54	—	−0.28*	−0.32*	−0.38*
Pb^{2+}	−0.18	—	−0.52*	−0.56*	Disappears*
Cd^{2+}	−0.62	—	−0.62*	−0.62*	−0.75*
Ni^{2+}	—	−1.01	−1.1**	−1.12**	−1.2**

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* pH 9.35.

** pH 2.5.

Results of the polarographic study of $\alpha, \alpha', \alpha''$-triaminedibenzyldiphenylmethanehexaacetic acid are given in Table 1.

It should be pointed out that the formation of a number of complex compounds occurs with this complexone with time; thus, at pH 9.35 the half wave potential is shifted from −0.6 to −0.76 volt, and the wave height decreases during this shift from 16 to 11 mm, and formation of a second wave is observed. After standing for five days $E_{1/2}$ for the first wave is shifted to −076 volt, while the second becomes well defined: $E_{1/2}$ −1.12 volt. These waves cannot be determined by stepwise reduction, since cadmium does not possess intermediate oxidation states. The most probable explanation for the appearance of these two waves is the formation of various complexes, the interconversion rate of which is so small that each complex gives its characteristic wave. After standing for a prolonged period (15 days) the second wave disappears and the potential for reduction of the cadmium ions becomes −0.7 volt. No more changes are observed on standing for a further period.

Such a phenomenon, presumably, can be explained by the presence of three complex-forming groups in $\alpha, \alpha', \alpha''$-triaminedibenzyldiphenylmethanehexaacetic acid, capable of forming intermediate complexes which react in succession.

Determination of the Instability Constant of Complexes of Certain Metals with Complexones

In order to get more complete characterization of the test complexones, the instability constants of their compounds with copper, bismuth, lanthanum, cadmium, cobalt, and nickel were determined by a polarographic method in acetate buffer solutions.

The experimental technique and the method of calculation have been described in detail in the work of Kolthoff and Lingane [2], Stromberg and Bykov [3], etc.

The following values were found for the instability constants:

For benzylaminediacetic acid:

$K_{Cu} = 1.32 \cdot 10^{-13}$ (pH 2.5; 4.4); $K_{Bi} = 7.42 \cdot 10^{-9}$ (pH 2.5).

For disodium benzhydrylaminediacetate:

$K_{Cu} = 8.9 \cdot 10^{-4}$ (pH 4.4); $K_{Co} = 1.26 \cdot 10^{-6}$ (pH 4.4); $K_{Ni} = 7.95 \cdot 10^{-7}$ (pH 2.5);
$K_{La} = 9.34 \cdot 10^{-3}$ (pH 9.35); $K_{Cd} = 2.76 \cdot 10^{-8}$ (pH 9.35).

For α, α', α''-triaminedibenzyldiphenylmethanehexaacetic acid:

$K_{Cu} = 1.86 \cdot 10^{-3}$ (pH 4.4); $K_{La} = 2 \cdot 10^{-5}$ (pH 9.35); $K_{Cd} = 1.82 \cdot 10^{-5}$ (pH 9.35).

Synthesis of Benzylaminediacetic Acid*

0.3 mole of benzylamine was added at 80° to 0.89 mole of monochloroacetic acid, neutralized beforehand with 5 N sodium hydroxide. Condensation was carried out for 5-6 hours at 105-110°. The filtered and cooled solution was acidified with 10% hydrochloric acid to a pH of 3. The white precipitate of benzylaminediacetic acid which separated out was filtered and carefully washed with water until a negative reaction was obtained for chloride ions. After recrystallization from butanol the compound obtained had a melting point of 201°.

Found %: C 59.16; 58.97; H 5.95; 5.84; N 6.28, 6.11.
$C_{11}H_{13}O_4N$. Calculated %: C 59.19; H 5.88; N 6.3.

Synthesis of α, α', α''-Triaminedibenzyldiphenylmethanehexaacetic Acid

16 g of α, α', α''-triaminedibenzyldiphenylmethane** was mixed with monobromoacetic acid neutralized with 29 % sodium hydroxide. Condensation was carried out under the same conditions as those described for benzylaminediacetic acid. The compound obtained was a white, amorphous powder with a yellowish tinge, it was readily soluble in alkali , hydrochloric acid, ethanol, but less soluble in butanol and isobutanol, it was insoluble in chloroform, acetone, and water.

Found %: C 61.28; 61.40; H 5.69; 5.70; N 5.46; 5.48.
$C_{39}H_{39}O_{12}N_3 \cdot H_2O$ Calculated %: C 61.69; H 5.35; N 5.46.

SUMMARY

1. Benzylaminediacetic acid and α, α', α''-triaminedibenzyldiphenylmethanehexaacetic acid have been synthesized and characterized polarographically.

2. A comparison of methylaminediacetic-, benzylaminediacetic , and benzhydrylaminediacetic acids, has shown that an increase in the molecular weight leads to a successive increase in complexing properties under certain conditions.

3. It has been established that α, α', α''-triaminedibenzyldiphenylmethanehexaacetic acid forms intermediate complexes with cations, these complexes being presumably the result of the presence of three complexing groups in this acid.

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* Benzylaminediacetic acid has been prepared previously by carboxymethylation of benzylamine.Leo W. Ziemlak, Jesse L. Bullock, J. Org. Chem. 15, 255 (1950).

** α, α', α''-triaminedibenzyldiphenylmethane was synthesized and kindly presented to us by I. G. Matveev and D. A. Drapkina.

*** Original Russian pagination. See C. B. Translation.

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APPLICATION OF OSCILLOGRAPHIC POLAROGRAPHY IN QUANTITATIVE ANALYSIS

COMMUNICATION 1. EFFECT OF ATMOSPHERIC OXYGEN DISSOLVED IN THE ELECTROLYTE ON THE VALUES OF THE CAPACITY CURRENT OF THE SUPPORTING ELECTROLYTE AND THE MAXIMUM VALUE OF THE CURRENT OF THE IONS BEING REDUCED

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In ordinary polarography, maxima of the first and second order appear on the current – voltage curves ($\dot{I} - \varphi$) [1], and these interfere with quantitative determinations. In order to suppress these maxima the usual procedure is to add surface active materials, which lead to a certain slowing down of the electrochemical processes, and to the development of "false" polarographic waves [1]. As an example of the development of such "false" polarographic waves, one can mention the polarograms obtained for Cd^{2+} in a supporting electrolyte of 1 N KCl at a gelatine concentration of 0.01%, using a Heyrovskii type polarograph in the absence of atmospheric oxygen. It is clear from Fig. 1 that after the limiting current for cadmium, there appears a sloping part on the curve (BC), which increases with decreasing Cd^{2+} concentration, and practically fuses into the diffusion current. Determination of the true limiting current for cadmium is very difficult.

No maxima are present in the case of oscillographic polarography, since just at the point where the drop has finished growing and when the oscillogram is taken, the movement of the surface slows down. It is also known that in ordinary polarography, the dissolved oxygen in the electrolyte has a considerable effect on the polarographic waves of the ions being reduced, and the presence of oxygen in the test solution interferes with quantitative determination.

In order to find out what is the effect of dissolved oxygen on $\dot{I} - \varphi$ curves when a saw-toothed voltage is applied to the cell, experiments were carried out on the separate and co-determination of Pb^{2+}, Cd^{2+}, and Zn^{2+} in a supporting electrolyte of 1 N KCl.

1 N KCl solutions, and the solutions of lead, cadmium, and zinc salts were prepared from spectrographically pure preparations obtained after several recrystallizations.

The solutions were electrolyzed on the Model No. 1 oscillographic polarograph of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry [2]. A constant (U=) and a saw toothed (U ~) potential were simultaneously applied to the electrodes of the electrolytic cell; the first was applied in order to diminish the effect of the capacity current on the maximum current of the ion being reduced (U ~ is the amplitude of the saw-toothed voltage).

In order to maintain the linearity of the saw-toothed voltage on the cell, the ratio of U= to U ~ is of essential importance. For U= / U ~ ≥ 1.0, there is no distortion of the saw-toothed voltage.

The electrolytic cell consisted of a slow dropping mercury electrode (dropping time τ = 14 - 15 seconds) and a mercury anode. The $\dot{I} - \varphi$ curves were registered for one drop of mercury of maximum size in the course of a few fractions of a second before it broke off, when the mercury surface remained practically unchanged. The values of the potential of the drop (φ_k) are given relative to the mercury anode.

In order to characterize the capacity current quantitatively, and its change with drop growth, as well as the effect of the electrochemical reaction on it, we turned our attention to the two following relationships: the results obtained will be considered in a special article [3].

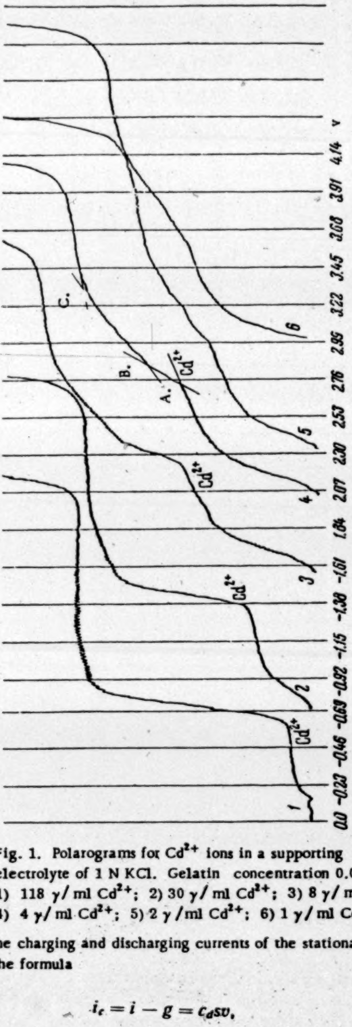

Fig. 1. Polarograms for Cd^{2+} ions in a supporting electrolyte of 1 N KCl. Gelatin concentration 0.01%.
1) 118 γ/ ml Cd^{2+}; 2) 30 γ/ ml Cd^{2+}; 3) 8 γ/ ml Cd^{2+};
4) 4 γ/ ml Cd^{2+}; 5) 2 γ /ml Cd^{2+}; 6) 1 γ/ ml Cd^{2+}.

The capacity current (the charging and discharging currents of the stationary double electric layer) on the growing drop is expressed by the formula

$$i_c = i - g = c_d s v, \qquad \text{(I)}$$

where i is the total current observed on the oscillogram; c_d is the differential capacity; v is the rate of change of potential in volts/second; g is the current for drop growth and s is the area of the electrode.

The current of the growth of the drop g is connected by a complex relation with calculated parameters. Right at the beginning of drop growth, the current g, and with it the total current i, increase strongly as compared with the capacity current, and give a clearly defined peak on the oscillogram. As the drop grows, the value of g rapidly decreases to some thousandths of the capacity current, and, for the oscillograms taken towards the end of drop growth, calculation of the differential capacity can be carried out sufficiently accurately by means of the fomula i/sv, i.e. by substituting the capacity current by the total current.

When an electrochemical reaction proceeds on the electrode, then the following relationship exists for the total current (for an arbitrary potential and for small amplitudes)of the saw-tooth voltage:

$$i = \frac{v(t-T/2)}{r_1+r_2} + \frac{vc}{(1+r_2/r_1)^2}\left[1 - \frac{(1+\lambda)e^{T-t/c(1/r_1+1/r_2)}}{e^{\frac{T}{c}(1/r_1+1/r_2)}+\lambda}\right] + g \ldots \qquad \text{(II)}$$

where T is the forward sweep time; t is the time (a variable); c is the capacity of the mercury electrode; r_2 is the electrolyte resistance; r_1 is the active part of the Faraday impedance; λ is the ratio equal to i(o)/i(T); i(o) is the current at the beginning of the sweep; i(T) is the current during the forward sweep T; λ is a characteristic of the apparatus.

A detailed expression for the current g is not of interest here, since at the point when the oscillogram is taken, it is insignificant as compared with the other two components.

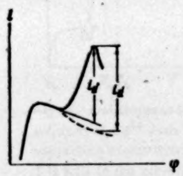

Fig. 2. The capacity current at the moment of reduction of the ion.

Using the formula it is possible to determine the diffusion current from the oscillogram.

Actually, if, at first glance, it would seem sufficient for determination of the diffusion current, to subtract the initial capacity current (vc) (Fig. 2) from the value of the total current (such a scheme is to be found in Delehay's book [4]), then from expression (II) it follows that the current determined in this way will be less than its true value, and this difference, even in dilute solutions, where r_1 is large, will exceed 5-10%. Actually, instead of the original capacity current (the fine line on the diagram) one should subtract the value, which is at least $\left(1+\frac{r_2}{r_1}\right)^2$ times smaller than it (the dotted line).

1. Electrolysis of 1 N KCl for Various Values of U = and U ~. On Fig. 3a are shown two oscillograms for 1 N KCl obtained for $U_= = -0.5$ volt; $U_\sim = 0.44$ volt; $U_{sweep} = 0.86$ volt and frequency (ν) = 17.5 cps. The potential of the drop was −0.94 volt. The first curve was registered in the presence of dissolved atmospheric oxygen, while the second was taken in the latter's absence. On the left is seen the sharp rise in the curve caused by

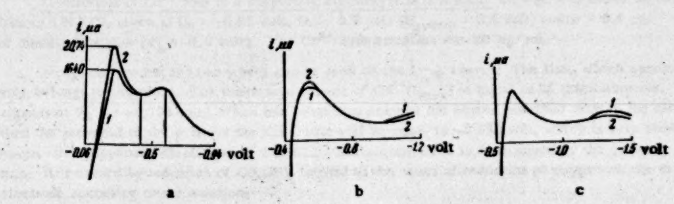

Fig. 3. Oscillograms for 1 N KCl:
a) $U_= = -0.5$ volt and $U_\sim = -0.44$ volt; $U_{sweep} = 0.88$ volt; b) $U_= = -0.8$ volt and $U_\sim = 0.4$ volt $U_{sweep} = 0.80$ volt; c) $U_= = -1.0$ volt and $U_\sim = 0.5$ volt; $U_{sweep} = 1.0$ volt.
1) In the presence of dissolved oxygen; 2) in its absence.

the charging current and by the form of the applied impulse. The maximum capacity current (i_c) is greater in the absence of oxygen than in its presence. For $\varphi_k = -0.24$ volt, the value of i_c has a maximum value, and on curves 1, 2 it is respectively equal to 16.4 and 20.74 microamperes (Fig. 3a). At more negative values of the potential of the drop, the capacity current gradually decreases, while for $\varphi_k = -0.40$ volt there is observed a small increase in the capacity current. Starting at a potential of −0.42 volt, curves 1 and 2 fuse into each other, while at a drop potential of −0.59 volt, there is again observed a sharp decrease in the current.

When the amplitude of the saw-tooth voltage is decreased, and the constant voltage on the cell is increased, the difference between oscillograms 1 and 2 (Fig. 3 b) becomes even less. For example, at $U_= = 0.8$ volt, $U_\sim = 0.4$ volt, $U_{sweep} = 0.8$ volt, oscillograms for 1 N KCl taken in the presence and absence of dissolved atmospheric oxygen practically coincide, with the exception of the peak for the capacity current which develops at $\varphi_k = -0.57$ volt. The maximum values of the capacity current on curves 1 and 2 are respectively 11.80 and 12.44 volt microamperes, which are 28-40 % less than the values of i_c obtained in the previous experiment. For $\varphi_k = -0.96$ volt there is observed a certain increase in the $\dot{I} - \varphi$ curves. In the potential range −1.0 to −1.2 volt, curve 1 is higher than curve 2. For $U_\sim = 0.5$ volt; $U_{sweep} = 1.0$ volt and $U_= = -1.0$ volt, curves 1 and 2 fuse into each other, and only in the range of φ_k −1.20 to −1.42 volt is there discernible a difference in the points, while the sloping increase on curve 1 is greater than the increase in curve 2 (Fig. 3 c).

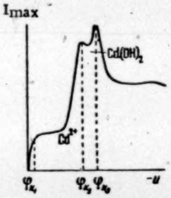

Fig. 4. Oscillogram for a solution of Cd^{2+} ions in a supporting electrolyte of 1 N KCl in the presence of dissolved atmospheric oxygen; $U_\sim = 0.2$ volt, $U_= = -0.8$ volt, and $U_{sweep} = 0.4$ volt.

Since, in ordinary polarography the first oxygen wave appears at about −0.1 volt, we tried to find this wave on the oscillographic wave in the same potential range. Experiment showed, however, that at $U_\sim = 0.02$ volt; $U_{sweep} = 0.04$ volt and $U_= = -0.08$ volt (i.e. for $\varphi_k = -0.1$ volt) there are no waves as the result of reduction of oxygen, while there is only a certain drop in the capacity current.

Thus, the effect of oxygen dissolved in the electrolyte on the oscillogram of 1 N KCl differs considerably from the effect of O_2 on a polarogram for KCl, on which is evident two clearly distinguished waves at φ_k −0.1 volt and 0.5--1.3 volt.

During electrolysis of solutions of KCl, KNO_3 and similar electrolytes, the presence of O_2 leads to a certain decrease in capacity current; this phenomenon only appears at the beginning of the oscillogram. Subsequently there is complete fusion of the $\dot{I} - \varphi$ curves up to $\varphi_k = -0.9$ volt, at potentials from −0.9 to 1.4 volt there occurs a sloping increase, which, in the presence of O_2 is somewhat greater than in its absence; finally, at more negative values of φ_k there is again a fusion of the curves.

Comparison of the curve $i_c - \varphi$ (on Fig. 3) with the curve relating the differential capacity of the mercury electrode and the potential in 1 N KCl [1, 5] shows that they are identical.

Electrolysis of Cd^{2+} ions in a supporting electrolyte of 1 N KCl. On Fig. 4 is shown an oscillogram for Cd^{2+} ions in 1 N KCl, taken at $U_= = -0.80$ volt, $U_\sim = 0.2$ volt ($U_{sweep} = 0.4$ volt) and $\nu = 6.4$ cps in the presence of dissolved oxygen ($\varphi_k = -1.0$ volt). The Cd^{2+} concentration was 20 μg/ ml.

A capacity current and two waves can be seen on the $\dot{I} - \varphi$ curves. The first, which appears at $\varphi^x_{k_2}$ * $= -0.765$ volt belongs to cadmium. The maximum current of Cd^{2+}(I_{max}) is equal to 75 microamperes. The second wave appears at $\varphi^x_k = -0.798$ volt. When one takes into account the ohmic potential drop in the circuit (0.086 volt), then the potential of the peak for the Cd^{2+} ions will be equal to −0.679 volt, which is very close to $\varphi_{1/2}$ for cadmium in a supporting electrolyte of 1 N KCl. The second wave is determined by the presence of oxygen in solution; it is caused by reduction of $Cd(OH)_2$ formed as the result of reduction of oxygen on the dropping mercury electrode accodring to the reaction:

$$O_2 + 2HOH + 2e \rightarrow H_2O_2 + 2OH^-,$$
$$Cd^{2+} + 2OH^- \rightarrow Cd\,(OH)_2.$$

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* $\varphi^x_{k_2}$ means that at a given potential a peak appears on the oscillographic curve.

The second wave disappeared on acidifying the solution with $HClO_4$.

As can be seen from Fig. 5, in the absence of dissolved oxygen, I_{max} for Cd^{2+} ions is greater than in the presence of O_2. The linear relation between cadmium concentration and the value of the maximum current is maintained both in the absence of O_2 as well as in its presence, which means that it is possible to carry out quantitative analysis without removal of dissolved oxygen from the test solution.

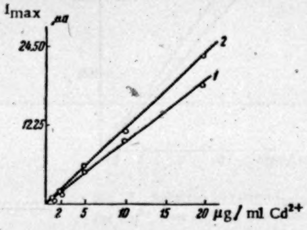

Fig. 5. Relation between I_{max} for Cd^{2+} ions and its concentration,
1) In the presence of dissolved O_2;
2) in the absence of O_2.
$U_= = -0.8$ volt; $U_\sim = 0.2$ volt and $U_{sweep} = 0.4$ volt.

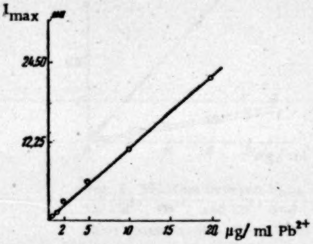

Fig. 6. Relation between I_{max} for Pb^{2+} ions and its concentration, in the presence and in the absence of dissolved atmospheric oxygen.
$U_= = -0.5$ volt and $U_\sim = 0.26$ volt.

3. Electrolysis of Pb^{2+} Ions in a Supporting Electrolyte of 1 N KCl. Electrolysis of 1 N KCl containing 20 μg Pb/ ml was carried out at $U_= = -0.5$ volt, $U_\sim = 0.26$ volt, $U_{sweep} = 0.52$ volt, and $\nu = 6.4$ cps in the presence, and in the absence of oxygen. The potential at which a peak appeared was −0.49 volt; taking into account the ohmic drop in potential in the circuit (0.05 volt) its potential becomes −0.44 volt, which is very close to the value of $\varphi_{1/2}$ for Pb^{2+} in the given medium. The value of I_{max} for lead in the absence and in the presence of dissolved oxygen remains practically unchanged.

Experiments carried out on the determination of different concentrations of Pb ions in a supporting electrolyte of 1 N KCl using the parameters indicated above, showed that oxygen dissolved in the electrolyte has no effect on I_{max} for lead. The relation between concentration and maximum value of the Pb^{2+} current is shown on Fig. 6. As Fig. 6 shows there is a linear relation between I_{max} and Pb^{2+} concentration in solution, both in the presence and in the absence of oxygen. The calibration curves practically coincide. Fig. 6 illustrates the possibility of the quantitative determination of lead in the presence of oxygen dissolved in the electrolyte.

4. The Effect of Dissolved Oxygen in I_{max} for Cd^{2+} Ions in a Supporting Electrolyte of 1 N KCl, in the Presence of Lead and Zinc. We thought it would be interesting to study the effect of dissolved O_2 on the maximum current of cadmium in the presence of other ions. To do this, two series of tests were carried out: in one series electrolysis of cadmium solutions was carried out in the presence of lead, while in the other it was carried out in the presence of Pb^{2+} and Zn^{2+}. The tests showed that in the presence of the accompanying ions, the wave caused by reduction of $Cd(OH)_2$ disappeared on the oscillographic curve (Fig. 4), and the effect of dissolved oxygen is reduced to a minimum (apparently, Pb^{2+} ions interfere with formation of $Cd(OH)_2$ in the layer adjacent to the electrode). The accompanying ions show a considerable effect on the value of I_{max} for Cd^{2+} ions. The increase in the maximum current of cadmium is less in the presence of lead, than in the presence of lead and zinc (Fig. 7).

A linear relation is also observed between the concentration and maximum current of cadmium in the presence of the accompanying ions. In normal polarography, during the simultaneous determination of two or several ions, in the absence of O_2, the other ions affect the limiting current of the ion being reduced [6].

5. Simultaneous Determination of Pb^{2+}, Cd^{2+}, and Zn^{2+} in a Supporting Electrolyte of 1 N KCl. Since, for analytical purposes, it is expedient to change the potential at the same rate, then for successive determination of lead, cadmium, and zinc, electrolysis of the test solution was carried out at a constant amplitude for the saw-tooth voltage of $U_\sim = 0.5$ volt. The constant voltage applied to the cell was changed from test to test. For determina-

tion of various concentrations of lead and cadmium in 1 N KCl a potential of $U_= = -0.4$ volt was applied, while for zinc $U_= = -1.0$ volt.

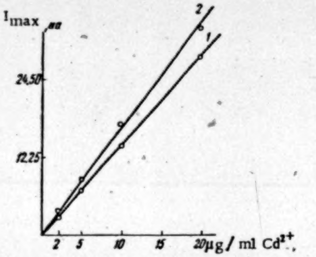

Fig. 7. Relation between I_{max} for Cd^{2+} ions and Cd concentration in the presence of Pb^{2+} and Zn^{2+}. 1) Cd^{2+}, Pb^{2+} ions in a supporting electrolyte of 1 N KCl. Obtained in the absence, and in the presence of dissolved O_2; 2) Cd^{2+}, Pb^{2+}, and Zn^{2+} ions in 1 N KCl; obtained in the absence and presence of dissolved O_2.

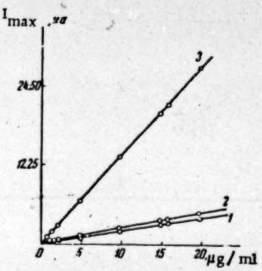

Fig. 8. Relation between I_{max} for Cd^{2+}, Pb^{2+}, and Zn^{2+} and their concentration when all are present simultaneously in a supporting electrolyte of 1 N KCl: 1) and 2) curves obtained in the presence and absence of O_2. At $U_= = -0.4$ volt and $U_\sim = 0.5$ volt; 3) obtained in the absence of dissolved O_2 at $U_= = -1.0$ volt and $U_\sim = 0.5$ volt.

For these values of the constant and saw-tooth voltages, the capacity current does not distort the oscillographic waves for Pb^{2+}, Cd^{2+}, and Zn^{2+}, when these ions are simultaneously present in the test solution.

The calibration curves for Pb^{2+}, Cd^{2+}, and Zn^{2+} ions coincide whether oxygen was present or not. The linear relation between the maximum value of the current for lead, cadmium, and zinc, and their concentrations in solution is shown in Fig. 8.

SUMMARY

1. Taking electrolysis of 1 N KCl as an example, it has been shown that the oscillographic curve of the supporting electrolyte is identical with the curve relating the differential capacity of the dropping mercury electrode and potential.

2. The presence of oxygen in the supporting electrolyte (1 N KCl) leads to a certain decrease in the capacity current at the beginning of the oscillogram. At more negative potential values dissolved O_2 has practically no effect on the $\dot{I} - \varphi$ curves.

3. When only Cd^{2+} ions are present in 1 N KCl, the dissolved O_2 decreases the value of the maximum current of cadmium, and, at a potential near to the potential for the Cd^{2+} peak, a second wave develops caused by reduction of $Cd(OH)_2$; this curve disappears on acidifying the solution.

4. The linear relation between concentration and the value of the maximum current of the ions being reduced is maintained, both in the presence and in the absence of oxygen dissolved in the electrolyte. This indicates that it should be possible to carrry out quantitative analysis without removal of O_2, and this is a real advantage over a ordinary polarography.

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THE USE OF THE MASS SPECTROMETER FOR ESTABLISHING THE RESOLVING CAPACITY OF CHROMATHERMOGRAPHIC APPARATUS

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Chromathermographic apparatus [1] has found wide application in gas analysis, in industry, and in scientific research work. In this connection it is important to establish the purity of the fractions obtained from a mixture of gases by the chromathermographic method by some independent method. We used the mass spectrometer for this purpose since it possesses a high sensitivity.

Results are given in the present article of work carried out by means of a MS-2 mass spectrometer in order to establish the purity of fractions obtained during separation of gas mixtures by chromathermographic apparatus (chromathermographs Nos. 4 and 5 and the universal chromathermographic apparatus).* Air is used as developer in chromathermograph No. 5 [2, 3] while the concentration of the separated component is determined beyond the adsorbent layer by means of a fixing apparatus based on measurement of thermal conductivity. Carbon dioxide is used as the developer in chromathermograph No. 4 [3]; the amounts of desorbed materials are measured visually in a nitrogen apparatus filled with 40% KOH solution.

The universal chromathermographic apparatus [4] is based on the simultaneous use of chromathermography, and partition and development chromatography. Air is used as developer, while registration is carried out on an apparatus based on measurement of thermal conductivity, or the thermal effect of combustion.

The unsaturated hydrocarbons used were prepared by dehydration at 360-400° of the corresponding alcohols on active alumina, the alcohols having been distilled three times beforehand.

The saturated hydrocarbons were prepared by hydration of the corresponding unsaturates on a nickel catalyst. The gases obtained in this way were purified from carbon dioxide.

The experimental technique employed was as follows: A known amount of the mixture of an appropriate composition was placed on the column packed with adsorbent, and separation effected by the simultaneous action of an air stream, or carbon dioxide, and by the moving electric oven. The time for separation of the individual components was determined, i.e., the retention volumes, under standard experimental conditions. Subsequently, separate fractions were sampled into glass ampoules from the chromathermograph through a three,way tap, and these fractions analyzed for purity on the mass spectrometer.

The following mixtures were analyzed: A) ethane — nitrous oxide — propane; B) methane — ethane — — ethylene — propane — propylene — butane — butylene on chromathermograph No. 5; C) methane — ethane — — propane — butane, and also natural petroleum gas on chromathermograph No. 4; D) methane — ethane — ethylene — propane — propylene — isobutane — n-butane — isobutylene — trans-butylene — cis-butylene — isopentane on the uiversal chromathermographic apparatus.

Fig. 1 illustrates the separation of a mixture of methane — ethane — propane — butane.

On Fig. 2 is shown the elution curve for a mixture of methane, ethane, ethylene, propane, propylene, isobutane, n-butane, isobutylene, trans-butylene, cis-butylene, and isopentane on the universal chromathermographic apparatus. The presence of ten discrete zones testified to the complete separation of the components.

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* Iu. I. Baranova, L. E. Pal'tseva, N. I. Fomicheva, and O. N. Iniushkina participated in the experimental work.

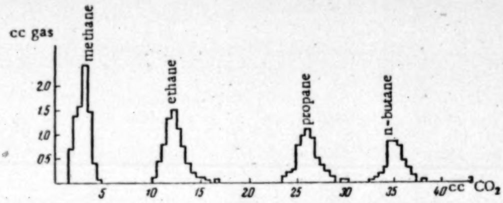

Fig. 1. Elution curve for separation of hydrocarbons on chromathermograph No. 4.

The apparatus used for establishing the purity of the gas fractions separated by means of the chromathermographic apparatus was the Russian MS-2 mass spectrometer which was provided with a system of adjustments enabling down to 0.01 cc of gas to be analyzed. The mass spectrum sweep was realized by automatically changing the field of an electromagnet. The mass spectra were recorded by an electronic potentiometer type EPP-09.

TABLE 1

Mass Spectra for Calibration of Propane*

Pressure in the system in mm Hg	Readings								Maximum error, absolute, %	Maximum error, relative, %
	1st	2nd	3rd	4th	5th	6th	7th	Mean		
	0.74	0.48	0.69	0.34	0.46	0.69	1.38			
Sensitivity in arbitrary units	5330	5720	5700	5550	5510	5710	6040	5640	–	7.1
Masses	As a % of the peak of mass 44									
26	33.7	34.5	34.0	34.6	33.9	33.7	32.7	33.9	1.2	3.5
27	141	143	140	144	139	138	142	140	3	2.1
30	7.9	8.7	9.5	9.6	9.6	7.2	9.58	8.8	1.6	18.2
39	71.8	71.2	70.1	69.2	68.6	67.9	67.9	69.5	2.3	3.3
41	49.2	49.1	48.4	48.7	47.6	48.7	48.5	48.6	1.0	2.1
42	21.6	22	20.6	21.7	21.3	21	21	21.3	0.7	3.3
43	88.7	87.8	88.7	88.0	88.0	87.8	88.1	88.1	0.6	0.7

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* All the mass spectra were taken in the course of one working day.

In order to check on the stability of the operation of the mass spectrometer, the calibration curves of the mass spectra were registered several times. Variations in the sensitivity of the mass spectrometer, and the ratios of certain peaks for propane and isobutane are given in Tables 1 and 2.

Calculations of the composition of the fractions were carried out by the sensitivity method suggested by Washburn et al [5, 6]. In order to increase the sensitivity of a determination, the content of an impurity was calculated on the basis of those peaks, on which the basic gas had no effect, or had a minimum effect, but on which the impurity showed the maximum effect. The peak with mass 28 was not used for calculation purposes since it had a high value in the background spectrum of the apparatus.

As an example we may quote the mass peaks used for determining impurities in the butane fraction: isobutane as impurity was determined on the basis of a system of equations compiled by using peaks with masses of 57 and 58; butylenes as impurities were determined using a peak with a mass of 56; propane as impurity on the basis of a peak with mass 44; propylene as impurity on the basis of a peak with mass 42; ethane on the basis of a peak with mass 30; ethylene on the basis of a peak with mass 26. In view of the small difference in the calibration spectra it was not possible to carry out a separate calculation for trans-butylene and cis-butylene.

TABLE 2

Mass Spectra for Calibration of Isobutane*

Pressure in the system in mm Hg	Readings									Maximum error, absolute, %	Maximum error, relative, %
	1st	2nd	3rd	4th	5th	6th	7th	8th	Mean		
	0.34	.45	0.68	1.36	0.31	0.41	0.61	1.22			
Sensitivity in arbitrary units	744	739	723	735	756	716	723	740	735	—	2.86
26	91	90	93	87.5	92.6	92.8	86	88	90	4	4.4
27	930	953	980	929	940	963	930	935	945	35	3.7
30	5.1	5.0	6.1	5.2	5.2	5.5	5.4	5.2	5.3	0.8	15.0
39	810	829	837	799	830	820	817	794	817	23	2.8
41	1700	1740	1770	—	1700	1720	1700	—	1720	50	2.9
42	1180	1260	1290	1240	1210	1240	1240	1230	1240	60	4.8
43	3930	4020	—	—	3980	4040	—	—	3990	60	1.5
56	24.0	24.0	23.2	21.2	23.0	22.0	21.0	20.0	22.3	2.3	10.3
57	130	130	132	131	130	130	129	129	130	2	1.5

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* All the mass spectra were taken in the course of one working day.

Table 3 contains the results obtained during analysis of fractions separated by means of chromathermograph No. 4.

TABLE 3

Analysis of Fractions Separated by means of Chromathermograph No. 4

Original mixture	Fraction designation	Composition of fraction, in %					
		i-C_4H_{10}	n-C_4H_{10}	C_3H_8	C_3H_6	C_2H_6	C_2H_4
C	Ethane fraction					99.1	0.9
	Propane fraction			99.9	0.1		
Natural gas from Well No. 23 (Mukhanovo)	Ethane fraction					99.9	0.1
	Propane fraction			99.9	0.1		
Natural gas from Well No. 67 (Mukhanovo)	Ethane fraction						
	Propane fraction			100		99.9	0.1
	Butane fraction	8.9	90.1		1.0		

As these results show, the ethane and propane fractions contain impurities, the amounts of which lie outside the limits of accuracy of determination by means of the mass spectrometer. The amount of butylene found as impurity in the butane fraction from natural gas obtained from Well No. 67 ("Mukhanovo" region), and amounting to 1 % (it is known that n-butane and isobutane are not separated on chromathermograph No. 4 when only one column packed with MSM silica gel is used), may also be explained by unstable readings of the mass spectrometer, since the natural gas does not contain butylene.

Thus, mass spectrometric analysis of fractions taken from chromathermograph No. 4 hardly detects any impurities at all in these fractions.

Table 4 contains results obtained during the study of fractions separated by means of chromathermograph No. 5.

It is clear from Table 4 that the propane and butane fractions from mixture A do not contain any impurities. The ethylene fraction contains 0.4 % ethane. The "nitrous oxide" fraction contains 0.1 % propane and 3.8 % ethane, from which it can be concluded that for this length of sorbent layer this fraction contains 96-97 % N_2O. 1.9 % butane was detected in the butylene fraction. The butane fraction from mixture B contains 0.2 % butylene; the propylene fraction contains 1 % propane; the ethylene fraction does not contain any impurities; 2-3 % of ethylene are contained in the propane and ethane fractions. The amounts of the impurities found in the individual fractions can either be explained by incomplete separation or by errors in determination on the mass spectrometer.

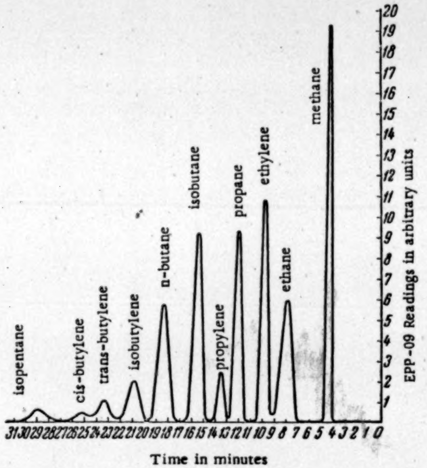

Fig. 2. Elution curve for the hydrocarbon mixture on the universal chromathermographic apparatus.

The results given in Table 4 therefore demonstrate that when chromathermograph No. 5 is used, practically complete separation of insaturated and saturated hydrocarbons is possible, since the small amounts of impurities detected by means of the mass spectrometer should not affect the peak heights on the elution curves.

TABLE 4

Analysis of Fractions Obtained by means of Chromathermograph No. 5

Original mixture	Fraction designation	Composition of fraction, in %							
		i-C_4H_{10}	n-C_4H_{10}	C_4H_8	C_3H_8	C_3H_6	C_2H_6	C_2H_4	N_2O
A	Nitrous oxide				0.1		3.8		96.1
	Ethylene fraction						0.4	99.6	
	Propane fraction				100				
	Butane fraction		100						
	Butylene fraction		1.9	98.1					
B	Ethane fraction						97.1	2.9	
	Ethylene fraction							100	
	Propane fraction				96.9	0.9		2.2	
	Propylene fraction				1.0	99.0			
	Butane fraction		99.8	0.2					

Table 5 contains the results of analysis carried out on the mass spectrometer of fractions taken from the universal chromathermographic apparatus. It is clear from the Table that here we have practically complete separation of proylene, isobutane, n-butane, and butylenes.

The authors wish to thank A. A. Zhukhovitskii for his valuable advice, and for the interest he showed in this work.

TABLE 5

Analysis of Fractions Obtained by means of the Universal Chromathermographic Apparatus

Original mixture	Fraction designation	Composition of fraction, in %						
		$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	C_4H_8	C_3H_8	C_3H_6	C_2H_6	C_2H_4
D	Propylene fraction					100		
	Isobutane fraction	97.9	0.5		1.6			
	n-Butane fraction		100					
	Butylene fraction			96.7	2.5			0.8

SUMMARY

A MS-2 mass spectrometer can be successfully used for periodic checking on the completness of separation of complex mixtures by the chromathermographic method, and also for choosing the optimum conditions for operation of chromathermographic apparatus.

Mass spectrometric analysis of fractions obtained during separation of gas mixtures on chromathermographic apparatus, shows that saturated and unsaturated hydrocarbons are completely separated on chromathermograph No. 4; in addition, when chromathermograph No. 5 is used, it is also possible to separate nitrous oxide from the hydrocarbons, while the universal chromathermographic apparatus permits resolution of butane isomers as well.

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DETERMINATION OF SODIUM AND POTASSIUM IN MINERALS BY FLAME SPECTROPHOTOMETRY

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At present alkali metals can be determined most accurately and swiftly by flame photometric methods. Appropriate procedures have been developed by us for the rare alkali metals — lithium, rubidium, and cesium — using an apparatus constructed on the basis of the universal UM-2 monochromator [1, 2]. It seemed desirable to develop similar methods for determining sodium and potassium on this type of apparatus.

A vast amount of work has been published relating to the determination of sodium and potassium in various materials, particularly in minerals, by means of flame photometry. The sample is usually put into solution by treating it with a mixture of hydrofluoric acid and sulfuric [3 - 6], or perchloric acids [7], and the solution is subsequently photometrically determined either by direct readings or by the method of addition [5]. Less often, fusion with calcium carbonate and ammonium chloride [8, 9] is used for opening up the minerals.

Of great importance during photometric determinations of solutions is the correct calculation of the mutual effect of the elements and the composition of the solution on the intensity of the radiation of the test element in the flame. Sodium and potassium mutually intensify the radiation of the other in an acetylene flame. Under such conditions, the radiation emitted by the sodium only increases weakly, while that of potassium increases strongly [10]. The reason given for this is the action of the atoms of one metal on the ionization of the other [11]; the intensity of the radiation of each element is proportional to the concentration of nonionized atoms in the flame, and as a result of suppression of ionization under the influence of the other element, the brightness of the radiation increases. The effect is not observed in the cold flame of a propane — air mixture [10, 12]. The relation between this effect and the flame temperature and concentration of the elements seems to be the reason for the fact that some authors have not observed the existence of this type of phenomenon [13, 14].

An effect of a different type is the decrease in radiation intensity caused by the presence of large amounts of acids or their salts; this probably leads to a slowing down of evaporation of the material from aerosol drops passing into the flame [15].

A general method of overcoming the effect of the composition of the solution on the intensity of the radiation of the test elements, is to choose standard solutions approximating in their composition to that of the test samples, or to make use of the so-called buffer action of the salts of certain metals on the radiation of the others [16].

The problem which formed the subject of the work described here was to check published results on the mutual effect of the elements, with a veiw to recommending a more suitable method of analysis.

Apparatus. The flame spectrophotometer used was constructed on the basis of a type UM-2 monochromator, and has been described previously [1]. A type FEU-19 photomultiplier was used as the receiver for the radiation when determining sodium, while for determination of potassium a type FEU-22 photomultiplier was used. The photocurrent was measured by means of a type "FI" mirror galvanometer, which had a sensitivity of 5×10^{-9} amperes/ mm of scale and an oscillation period of 7 seconds. When an illuminating gas flame was used, the burner was a glass one similar to that used for acetylene flames; it differed, however in the diameter of the outlet opening which was 10 mm (Fig. 1).

The supply of illuminating gas was thereby cut down until a small flame with a sharply defined inner cone was obtained.

For characterizing the suitability of the apparatus for determining sodium and potassium, the values of the "specificity factors" [1] were determined during determinations of these elements in the presence of others which radiate in the flame. As pointed out already, the "specificity factor" is a number which shows how much of another (foreign) element can be present in order to give the same galvanometer reading as the test element at a concentration of 10 γ/ml. A reading is given by the foreign element because of the radiation of the foreign element by another wave length scattered by the monochromator, or by the radiation of a molecular band of the same wave length. Because of the presence of sodium and potassium salts as impurities in test preparations of foreign elements, during the determination of specificity factors, in order to get readings at the sodium wave length (589 - 590 mμ), or at the potassium wave length (766 - 770 mμ), readings were taken in the spectrum region on both sides of these lines and the results interpolated to the given wave lengths.

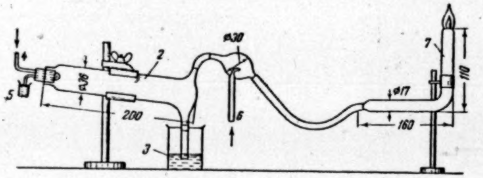

Fig. 1. Sprayer and burner for working with illuminating gas.
1) Sprayer; 2) spraying chamber; 3) discharge of excess solution; 4) compressed air supply; 5) test solution; 6) inlet for illuminating gas; 7) burner.

The results obtained are given in Table 1.

TABLE 1

Approximate Values of Specificity Factors during Sodium and Potassium Determinations

Element	Sensitivity, in γ / ml/ division	Specificity factors in the presence of				
		Na	K	Li	Ca	Sr
Sodium						
Illuminating gas flame	0.005	–	275000	> 40000	11000	–
Acetylene flame		–	> 150000	> 15000	3800	20000
Potassium						
Illuminating gas flame	0.01	> 100000	–	> 10000	> 100000	> 100000
Acetylene flame	0.01	180000	–	> 18000	15000	15000

The slit width (inlet and outlet) was 0.1 mm.

These results demonstrate the high quality of the photometer constructed for sodium and potassium determinations. When an acetylene flame was used, sodium radiation was observed, this was presumably caused by the presence of sodium in the glass of the burner, nevertheless, it only corresponded to a total content of 0.3 γ of sodium/ ml in the solution, and it did not interfere with the work.

Sodium Determination. Since it was intended to determine sodium and potassium at contents of these elements up to 10 % in a test sample, during photometric determinations on solutions with concentrations (calculated on the sample) of 1 mg/ ml, it was necessary to establish the conditions for determining sodium at concentrations of this element in solution up to 100 γ/ ml. The relation between radiation intensity and concentration in the range 0 - 100 γ/ ml curves toward the abscissa (Fig. 2), while the curves obtained for an acetylene flame and for an illuminating gas flame practically coincide, as long as the maximum intensity of the radiation for a solution with a concentration of 100 γ/ ml is taken as 100 in both cases.

Direct proportionality between concentration and readings is only observed up to 10 γ / ml (Fig. 3), in the range 40-100 γ/ ml the readings are proportional to the square root of the concentration.

Despite the absence of a direct proportionality in the range 10 - 100 γ/ ml, sodium can be determined with reasonable accuracy by making comparisons with two standard solutions approximating in concentration to the test solution.

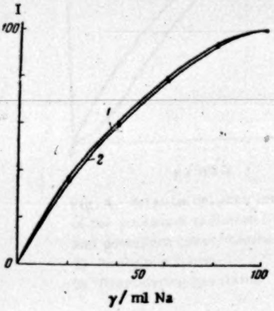

Fig. 2. Relation between radiation intensity of sodium (0 - 100 γ/ ml) and its concentration in solution.
1) Acetylene flame; 2) illuminating gas flame.

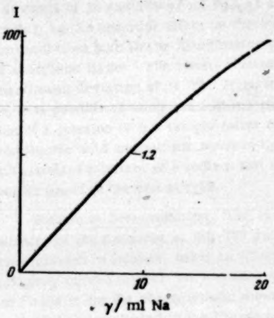

Fig. 3. Relation between intensity of sodium radiation (0 - 20 γ/ ml) and its concentration in solution.
1) Illuminating gas flame; 2) acetylene flame.

In order to establish the effect of elements which accompany sodium in minerals, photometric measurements were carried out on solutions which were 0.025 N. with respect to hydrochloric acid, and containing in addition to sodium at a definite concentration, calcium, aluminum, potassium, and phosphates in amounts which may be expected to be present in samples. The readings obtained in these experiments were compared with the readings obtained for a solution of sodium salt of the same concentration, but without additions of foreign elements. In adddition, solutions of mixtures of the added materials were also measured photometrically, and the readings obtained subtracted from the readings for the solutions of the sodium salts to which the foreign elements had been added. Comparisons were made of the results obtained with both the acetylene flame and the illuminating flame.

TABLE 2

Errors During Determination of Sodium in a Solution Containing Additions of Foreign Elements

Sodium content of solution in γ / ml	Foreign elements added, in γ / ml				Error in comparing with a solution not containing sodium, in %	
	Al_2O_3	CaO		P_2O_5	In illuminating gas flame	In an acetylene flame
10	—	500	100	—	−1.6	+3.4
40	500	—	100	—	−1.9	−3.6
80	500	500	100	—	−1.2	−2.3
10	—	—	—	10	0	+0.6
10	500	500	100	10	−2.2	+4.3
10	—	—	—	100	+2.9	+0.7
10	500	500	100	100	+1.3	−1.2
50	500	500	100	10	−0.6	+1.5
50	500	500	100	100	−1.7	−1.5
50	—	—	—	100	+1.7	−1.5
50	—	—	—	10	+1.2	−1.5

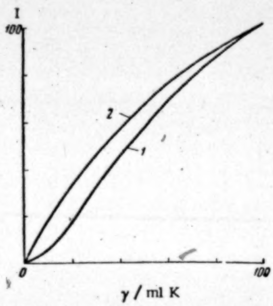

Fig. 4. Relation between intensity of the potassium radiation (0-100 γ ml) and potassium concentration.
1) Acetylene flame;
2) Illuminating gas flame.

As the results given in Table 1 show, addition to solutions of sodium containing 10 to 80 γ/ ml of sodium (these correspond to concentrations of 1.0 - 8.0% in the test sample), of aluminum and calcium in amounts up to 500 γ/ ml of the oxides (50% in the test sample), of potassium in amounts up to 100 γ/ ml (10% in the test sample), and of phosphates in amounts of 10 and 100 γ/ ml P_2O_5 (1 and 10% P_2O_5 in the sample), has no essential effect on the intensity of the sodium radiation both in the illuminating gas flame, and in the acetylene flame. The results obtained for sodium showed a maximum deviation of ± 3%. Thus, in the case of sodium, it is possible to carry out a direct photometric comparison of a solution of test sample (after decomposition with hydrofluoric acid and sulfuric acid) in hydrochloric acid, with standard solutions of a sodium salt free from the components found in the test sample.

Potassium Determination. The curve relating the intensity of the radiation at 766-769 mμ and potassium concentration in solution, using an illuminating gas flame, is slightly curved toward the abscissa, while for an acetylene flame it has the characteristic drawn out S shape (Fig. 4) which has been noted in the literature.

On plotting the curves on logarithmic paper it is clear that the radiation intensity is only directly proportional to the concentration in the range 40-60 γ/ ml; in the range 5-40 γ/ ml it is proportional to the concentration raised to the order of 1.33, while in the range 60-100 γ/ ml it is proportional to concentration raised to the order of 0.77. The presence of the initial part of the curve, in which there is observed a more rapid growth of radiation intensity with increasing concentration in the hotter flame of acetylene, can be explained as resulting from ionization of the potassium. Under such conditions, in accordance with the equation $K \rightleftharpoons K^+ + e^-$ (e^- is the electron), part of the potassium is already ionized and cannot give the radiation of the resonance line of potassium 766.6 - 769.0 mμ, which is determined by the transfer of electrons into the neutral potassium atoms. The concentration of ionized potassium atoms is determined by the equation

$$\frac{[K^+][e^-]}{[K]} = \text{const},$$

where (K) , (K^+) , and e^- are the concentrations in the flame, of atoms and ions of potassium, and of electrons respectively. Since K^+ and e^- are equal, then from this $\frac{[K^+]^2}{[K]}$ = const. Denoting the concentration of the atoms in the flame in the absence of ionization by N, we get $[K^+] + [K^+] = N$; $[K^+] = N - [K]$ n $\frac{N - [K])^2}{[K]}$ = const. Transforming this gives $[K]^2 - 2N[K] + N^2 - \text{const}[K] = 0$, from which it is clear that the concentration of nonionized atoms in the flame is determined by the root of an equation of the second degree representing a parabola. The initial part of the curve relating radiation intensity and concentration, is, in shape actually reminiscent of a parabola.

The equation for ionization equilibirum $\frac{[K^+][e^-]}{[K]}$ = const can explain the following regularities relating to the mutual increase in the radiation intensity of the alkali metals.

1. Readily ionizable metals (rubidium, cesium) should have a greater effect than less readily ionizable metals (such as lithium), since they should displace the equilibrium to a greater extent by supplying a greater concentration of electrons.

2. The intensifying effect of other metals should be strongest of all at low potassium concentrations, since, under such conditions, a relatively large part of the potassium atoms will be ionized.

3. The increase in potassium radiation on addition of another metal in increasing amounts will tend to a limit, which will be determined by complete suppression of the potassium ionization, and the limit will be reached sooner, the lower the ionization potential of the metal added.

4. The intensification of the radiation will be stronger in flames where a large part of the atoms will be ionized, i.e. in flames with higher temperatures.

TABLE 3

Effect of Sodium on Potassium Radiation

K, in γ/ ml	Radiation intensity in % on addition of Na, γ/ ml				Gas used
	0	4	20	100	
4	100	101	117	157	Acetylene
10	100	—	112.7	131	—,—
40	100	—	100.5	107	—,—
1	100	—	—	113	Illuminating gas
2	100	—	—	113	—,—
4	100	101.8	103.6	105.5	—,—
10	100	—	102.0	93.6	—,—
40	100	—	101.0	100.0	—,—

The experimental results given below illustrate the points made above, namely points 1 - 4. Table 3 contains results on the effect of sodium salts in various flames on the intensity of potassium radiation. As these results show, in the case of acetylene flames, when small amounts of potassium are involved, sodium in concentrations up to 100 γ/ ml leads to an increase in the intensity of the potassium radiation of about twice its real value, while at potassium concentrations of 10-40 γ/ ml the effect is already becoming small. Changing over to an illuminat-nating gas flame practically completely eliminates the effect. It follows from this last fact that in an illuminating gas flame, potassium can, apparently, be determined at concentrations which are not too small, i.e. in amounts greater than 2-3 γ/ ml, by comparison with standard solutions free from components present in the test material.

TABLE 4

Errors arising during Determination of Potassium in Solutions which are 0.25 M with Respect to HCl and contain test components, when Illuminating Gas and Acetylene Flames are used, and Sodium is Added to the Solutions

K content in solution in γ /ml	Test components added, in γ /ml					Error on comparison with an Na-free sol. %	The same with an acetylene flame (add. of Na), %
	Al_2O_3	CaO	MgO	Na	P_2O_5		
4	500	500	100	100	—	+1.8	—2.5
50	500	500	100	100	—	—2.0	0
50	—	—	—	—	10	0	—1.5
50	—	—	—	—	100	0	—2.0
4	500	500	100	100	10	—3.5	—1.5
4	500	500	100	100	—	+1.2	0

Table 4 contains results for potassium determinations in solutions containing test components (using an illuminating gas flame).

We shall return below to the results given in the last column, while for the moment we note that during work with low temperature illuminating gas flames, additions of components of the test material in amounts corresponding to 50% Al_2O_3, 50 % CaO, 10 % MgO, 10 % Na and 10% P_2O_5 (for an ore sample of 1 mg/ ml of solution) do not affect the value of the readings, and permit one, as in the case of sodium, to carry out a direct comparison with a series of standard solutions.

As for the acetylene flame, in this case, analytical procedure must take into account the effect of sodium on the intensity of the potassium radiation, and this effect must be compensated for accordingly. The simplest procedure would be to use the buffering action of sodium salts, added in excess to standard solutions and to test solutions [16]. Actually, at sodium concentrations in the solution of 1-2 mg/ ml, the intensity of potassium radiation increases little with increasing sodium concentration (Table 5).

TABLE 5

Relation Between Intensity of Potassium Radiation and Sodium Concentration of the Solution

K concentration, in γ/ ml	Radiation intensity on addition of various amounts of Na, in mg/ ml						Note
	0	0.1	0.5	1.0	2.0	5.0	
10	100	131	148	171	—	178	in0.25 *M* HCl
5	100	156	—	192	196	197	
40	100	107	114	120.6	126.3	125	
100	100	100.9	101.3	102.1	102.5	101.2	

On addition of sodium in amounts of 2 mg/ ml to standard and test solutions, the normal components of the test material, as can be seen from the last column of Table 4, do not interfere. The same is true when cesium (20 γ / ml Cs_2O) and rubidium (10 γ/ ml Rb_2O) are added; this means that the method can be applied for analyzing test materials containing small amounts of these elements.

Recommended Experimental Procedure. Below is given a description of the procedure published in the literature [4], which has been modified in accordance with the results obtained during the present investigation.

Solutions Required:

1) Stock solution of sodium and potassium containing 1 mg/ ml of the metal; 0.5084 g of calcined sodium chloride and 0.3814 g of potassium chloride were dissolved in good quality distilled water in a 200 ml standard flask (twice distilled water may be used) and the volume made up to the mark.

2) 5 N hydrochloric acid.

3) 10 % sodium chloride solution (for potassium determinations in an acetylene flame); 1 ml of solution contains about 40 (39.3) mg of sodium. The sodium chloride used for this purpose should contain as little potassium as possible. The marketed product should be purified by recrystallization. A saturated solution of sodium chloride should be prepared by heating, the solution is filtered and then the sodium chloride precipitated by addition of concentrated hydrochloric acid. On cooling, the sodium chloride is filtered off, washed with hydrochloric acid 1 : 1; purification by recrystallization is then repeated.

4) Standard Solutions. For use during determination of sodium and potassium in an illuminating gas flame, and determination of sodium in an acetylene flame. The amounts of the stock solutions of sodium and potassium salts given in the table below, are mixed with 5 ml of 5 N hydrochloric acid in 100 ml standard flasks and the volume made up to the mark.

Number of the standard solution	1	2	3	4	5	6	7
Na(K) content, in γ/ ml	0	10	20	40	60	80	100
Amount of stock solution, in ml	0	1	2	4	6	8	10

When standard solutions to be used for determination of potassium in an acetylene flame are prepared, 5 ml of a 10 % solution of sodium chloride is also added to the contents of the flasks.

5) Hydrofluoric and sulfuric (1 : 1) acids — reagent grade.

An accurately weighed aliquot of mineral equal to 0.1000 g is treated with 5 ml of hydrofluoric acid and 1 ml of sulfuric acid (1:1) in a platinum crucible, the mixture is heated on a sand bath, first gently, and then more strongly, and evaporated practically to dryness. It is allowed to cool, and then 5 ml of 5 N hydrochloric acid and 5-10 ml of water added to it. The mixture is heated to dissolve the salts. It is cooled again, and, in case where an illuminating gas flame is to be used, it is diluted to the mark in a 100 ml standard flask. This solution is then measured flame photometrically, first for one element (sodium) and then for the lines of the other element (potassium), a comparison being made with two adjacent standard solutions, one of which gives a higher reading, and the other a lower reading than the test solution.

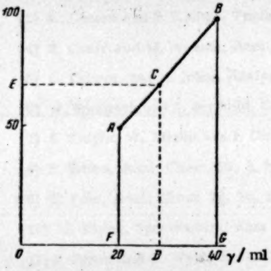

Fig. 5. Calculations of the content of an element in a test solution: AF and BG) readings for standard solution; OE - CD) reading for test solution; OD) content of element in test solution.

When an acetylene flame is used two test solutions are necessary — the one for determination of sodium is prepared as described above, while the other, which is used for potassium determination, contains 2 mg/ ml of sodium. When it is not desirable to prepare separate solutions from two separate aliquots of sample, the solution obtained as described above, after decomposition of the sample with hydrofluoric acid and sulfuric acids, and subsequent treatment of the residue with hydrochloric acid, is diluted to 50 ml in a standard flask. 10.0 ml of this solution is taken for determination of sodium, this 10.0 ml being diluted with an equal volume of water in a dry beaker. Other 10 ml lots of the same solution which are mixed with 1 ml of 10 % sodium chloride solution and 9 ml of water are then used for potassium determination; the final solutions obtained being compared with standard solutions containing the same amounts of sodium.

Readings are taken for test solution and for two adjacent standard solutions, one of which gives a higher reading, and the other a lower reading than the test solution. The readings are repeated in the reverse order and the mean values taken. Calculation is carried out graphically. The calibration curves are obtained by plotting concentration of test element in γ/ ml on the abscissa, and the galvanometer readings on the ordinate. The points corresponding to the two standard solutions are plotted on the graph and connected by a straight line. An intercept corresponding to the reading obtained for the test solution is marked out on the ordinate, a straight line is then drawn from this point on the ordinate parallel to the abscissa (Fig. 5) to intersect the line connecting the two points for the standard solutions; a perpendicular is dropped from the point of intersection on to the abscissa. The value of the intercept on the abscissa, taken from the origin, then gives the content of the element in the test solution. The value found for the content of the element in γ/ ml divided by 10 gives its content in the test sample in %.

For determination of potassium and sodium it is necessary to use reagents containing the minimum amounts of the alkali metals. It is best to use twice distilled water. Standard solutions should be prepared immediately prior to determination, so as to avoid contamination by alkali metals, which may come from the glass of the flasks used. A blank must be carried out, and the necessary corrections applied.

SUMMARY

Conditions have been established for the flame photometric determination of sodium and potassium in minerals, using an apparatus constructed on the basis of the universal UM-2 monochromator. It has been found that such an apparatus ensures high sensitivity and specificity for determination of sodium and potassium. A study which has been made of the effect of accompanying elements on the radiation intensity of sodium and potassium in two flames — illuminating gas and acetylene — has made it possible to choose conditions whereby these metals can be accurately determined whichever flame is used.

Experiments carried out on synthetic mixtures have shown that determination of the alkali metal content in the range 0.4 - 8.0% is possible with an accuracy of ± 3%. Explanations have been given for some of the phenomena observed, namely for the shape of the curve relating radiation intensity and concentration, and for the nature of the increase in potassium radiation intensity in the presence of sodium, the explanations being based on the ionization of the elements in the gas flames.

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AN ARC LAMP FOR EMISSION SPECTROGRAPHIC ANALYSIS OF POWDERS

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Direct current carbon arcs have hitherto been mainly applied for analyses not requiring a high degree of accuracy, on account of insufficient reproducibility. The search for methods of improving the accuracy obtained when using a dc arc is of great practical importance. With this aim in view some techniques have been developed for the uniform introduction of the test material into the evaporation zone of the arc [1]. In order to eliminate the causes which give rise to these errors, it has been found necessary to isolate the arc from the surrounding space by placing it in a protective atmosphere of an inert gas. Until recently, such light sources have been predominantly used for scientific research. The cells used for this purpose are relatively simple and are characterized by an appreciable consumption of inert gases [2-4].

In developing a cell for series analyses we had in mind above all the problem of cutting down on the amount of the gases used for creating an inert atmosphere. In addition, the construction of the cell should be such that it would allow rapid assembly and handling during changing of electrodes and samples.

The amount of gas used was cut down by using the same gas several times, this being achieved by forced circulation of the gas in a closed system, consisting of the cell, a system of filters for purification,and a pump.

During the development of this apparatus the individual parts of the setup were modified several times. The cell used at the moment is that depicted on Fig. 1. It was designed for use with test material, either prepared in the form of heat resistant mouldings, or placed in the canal of a carbon tube with a small diameter – the so-called "straws" 1 [1]. The arc burns in the small space 3 between electrodes 2 and 5. The whole setup is divided into an upper and lower part by the base 29. The upper part, in turn, consists of two detachable parts. By means of stands, not shown in the diagram, the elements of the upper part are fastened together, and to the base by bayonet connections. The joints are packed with gaskets 23 and 28. The test sample 7 is fixed in clamp 10; it is centered along the axis of electrode 5 by the projecting part of detail 9. This detail is electrically insulated from the other parts and has a flange for better removal of heat from its upper working part. The lower electrode is fixed in a hollow in the base 29 by light compression.

The arc is struck by bringing the electrodes into contact. Both during the time of preliminary firing, and during photographing of the spectra, the sample is continuously and uniformly fed into the canal of the lower electrode 5. The mechanism used for ensuring this uniform supply of sample into the arc (this mechanism is not shown on the diagram) makes it possible to regulate the lifting of the molding at a uniform speed of 0.01-0.10 mm/second. The movement from the supply mechanism is transmitted by the coupling rod 11, which is fitted with a gasket 13 at the place where it comes out. Technical nitrogen is fed at a rate of about 1 ml/second into the electrode canal at the same time as the sample. Sweeping of the electrode surface by the gas favors complete transfer of the vapor of the test material into the gap and ensures more stable burning of the arc. The gas used for sweeping, which is passed through a canal in the base 29 (not shown on the diagram) passes into space 8, and, after passing through a series of distribution points in detail 9 appears on the surface of the electrode.

A considerably larger amount of gas is used for sweeping the cell in which burning takes place 3. The gas used for this purpose passes through a separate canal in base 29 into the distribution cell 30, from which it passes through 24 small openings arranged on the periphery of the electrode base in the form of gas jets flowing together;it then passes into the firing cell where the discharge flows along the periphery from all sides. In order to create

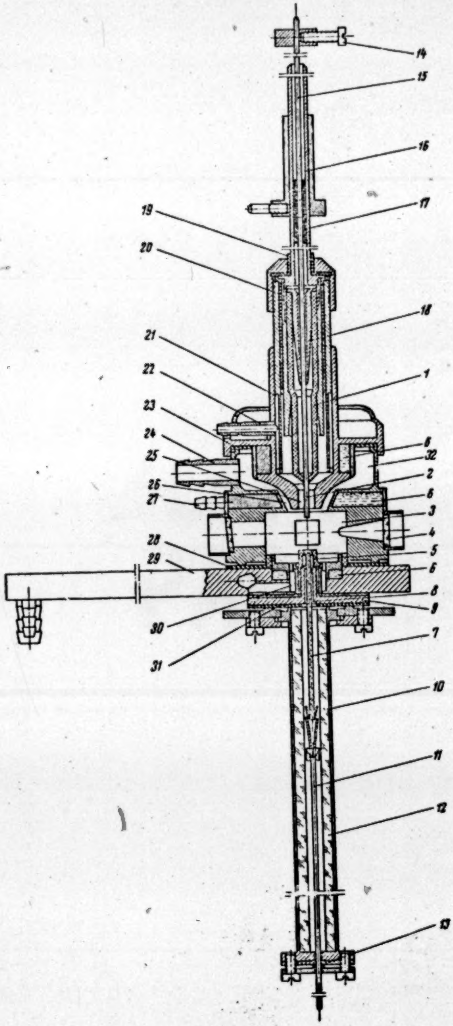
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Fig. 1. Arc lamp for spectrographic analysis of powders.

the conditions under which the gas sweeps the arc in the best possible way, the annular gap 26 also participates, through this gap, the gas together with the discharge products are sucked from the cell. Sweeping of the arc creates the best conditions for the passage of the radiated arc light through the upper, colder layers of the arc discharge. Nitrogen, argon, and helium were tested for production of a protective atmosphere. For daily work nitrogen was used, this gas being introduced into the system at the rate of 100 ml/ minute. Excess of the gas formed in the set up is lead away through a ventilator. Thus only part of the gas circulating through the cell is renewed after each cycle.

The discharge cell is fitted with four quartz windows, through one of which 4, the light is directed onto the spectrograph slit. The window is separated from the cell by comparatively narrow and deep niches, which decrease the possibility of formation of deposit from particles of condensed test material. The efficient gas sweep and the niches permit the window to be brought appreciably nearer to the arc, and this in turn means that it is possible to decrease the size of the whole setup. The use of water cooling 6 for all those places which are subjected to the action of the hot arc also favors the use of a smaller apparatus. The gas sucked out of the discharge cell passes into the intermediate cell 32, from which it is directed through nipple 24 into the filter used for its purification.

The upper electrode 2 is in the form of a carbon rod 1 mm in diameter and about 15 cm long. The use of a current of 6-7 amperes with such a thin electrode meant that it was necessary to develop a special apparatus in order to maintain the mobility of the electrode. The electrode itself is fastened in a metal case by means of clamp 17. The upper part of the mounting 15 can be connected with a stay which is connected with the feed mechanism of the upper electrode (not shown on the diagram). Using this mechanism, the arc is struck, and the arc distance is kept constant. Every time the upper part of the setup is dismounted (for recharging) the connection between the electrode and the feed mechanism is destroyed, to do this it is sufficient to free screw 14, and, by turning the stay take it out of the engagement. The current to electrode 2 is supplied by a system of six graphite brushes with a crosss section of 1 x 0.5 mm. Each brush is a component part of an elastic graphite attachment (1). The degree of pressure applied to the brush is regulated by rotating a band the conical shoulder of which, resting in the shoulder of the attachment, ensures their displacement towards the center.

All the details of the upper electrode are electrically insulated from the remaining parts of the setup by means of the ebonite details 19 and 20. The electrode is not changed until it has been used up. In practice, for photographing one spectra for a long burning period of the arc of 4 minutes, not more than 3 - 4 mm of the electrode is used up.

Part of the gas circulating in the system passes into the discharge cell from the side of the upper electrode, and prevents condensation of the vapors of the test material on the cold parts of the electrode. For this purpose, the gas passes into the distribution cell 21 through nipple 22, and from there, through several openings, into gap 25.

The use of an unusually thin upper electrode with a diameter of only 1 mm is not accidental. It is known that the shift of the cathode spot strongly affects the shape and dimensions of the radiating arc cloud. The only possible way of stabilizing the position of the cathode spot is to keep the operating part of the electrode at a sufficiently high temperature. The normal method, which consists in sharpening a comparatively thick electrode, does not answer this requirement, since, as it burns out and becomes blunt, the amount of heat removed from the sharpened part increases, the temperature drops, and the spot begins to shift. Nevertheless, if one takes electrodes with a decreasing diameter, then at some cross section it is possible to obtain a position such that the burning out of the electrode does not lead to an increase in the amount of heat which is removed from the operating part. A further decrease in cross section is not desirable, since the electrode wears out more rapidly on account of overheating.

For a 10 amperes arc, operating in air, the critical diameter of the electrode is about 2 mm. For a closed arc operating at 6 - 7 amperes, in an atmosphere of technical nitrogen, it is 1 mm. The shape and dimensions of the lower electrode were chosen so that they would ensure a stable spindle-shaped discharge.

When work is carried out in a protective atmosphere, the lower electrode maintains its dimensions for a long time, thereby ensuring a stable regime for arc burning. As for the upper electrode, the insignificant amount of wear which this electrode undergoes has no effect on the arc regime, since the distance between the electrodes is kept constant.

Realization of a continuous and uniform supply of test material into the discharge is one of the most important factors ensuring stable excitation conditions during the whole time of the exposure. Thus, in the apparatus described, many of the reasons, which in the case of other light sources would have led to the break down of evaporation conditions of the test material, and of the excitation of its spectrum, have been eliminated. More favorable conditions have also been created for the passage of the radiation through the absorbing regions of the discharge.

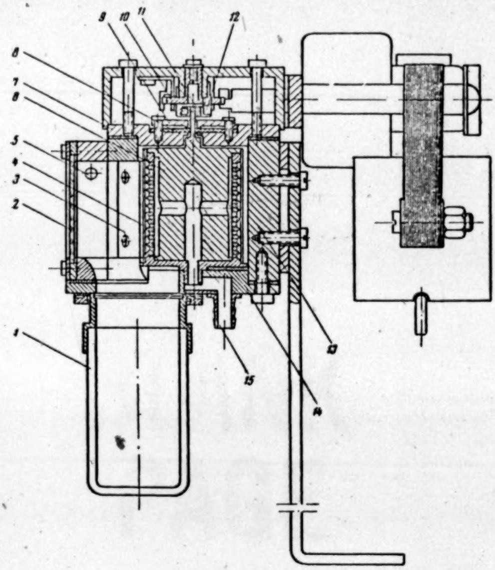

Fig. 2. Gas filter.

For its capacity of giving a prolonged stable radiation, the source of light obtained has been called an arc lamp. This is not a new term in technics; it is, however, new in the field of emmission spectrographic analysis, since closed sources of light with a continuous supply of test material are not known.

On the one hand, working with a closed arc has still one further advantage, namely that it completely excludes the effect of the variable factors of the surrounding atmosphere (composition, contamination, presence of currents); while on the other hand, the use of an arc lamp is not accompanied by the appearance of any disadvantages, and, in particular, no more time is spent in changing electrodes and samples than in other systems.

For ensuring normal operation of an arc lamp a number of setups are used, in particular, the mechanisms for adjusting the upper electrode and for supplying the sample (moldings or "straws"). Of special importance is the filter used for purifying the gas, and the pump used for circulating the gas in the lamp system.

The construction of the filter is shown on Fig. 2; the filter consists of a grooved drum around which a roll of filter paper 4 is wrapped. The drum is placed in a hermetically sealed cell and is slowly rotated by means of a Warren motor. The gas to be purified is passed through opening 5 ,and, after passing through the filter paper, is freed from solid impurities. Subsequently, having passed the openings into the drum grooves, the gas passes into the central canal of the drum, and passes out of the filter through nipple 15 . The part of the deposit forming on the drum is cut out with knife 3 and falls into bunker 1 ,from which it can be removed when necessary. The remaining thin layer of deposit plus the filter paper forms the filtering element of the setup. Window 2 enables one to follow the work of the filter.

A pump is used for sucking out the gas used in the arc lamp, for propelling it through the filter, and compressing it for repeated use. Normal laboratory or industrial pumps could not be used for this purpose since they do not satisfy the requirements. The efficiency of the pump needed for the lamp is not high and need not exceed 1 liter/ minute; it should supply an uniform gas flow. The construction of the pump used for the work is shown on Fig. 3. The electric motor 14 rotates an intermediate shaft with an eccentric 13. The latter is connected through a coupling rod to a piston 11. The gap between piston and cylinder 1 is covered by a bellows 12.

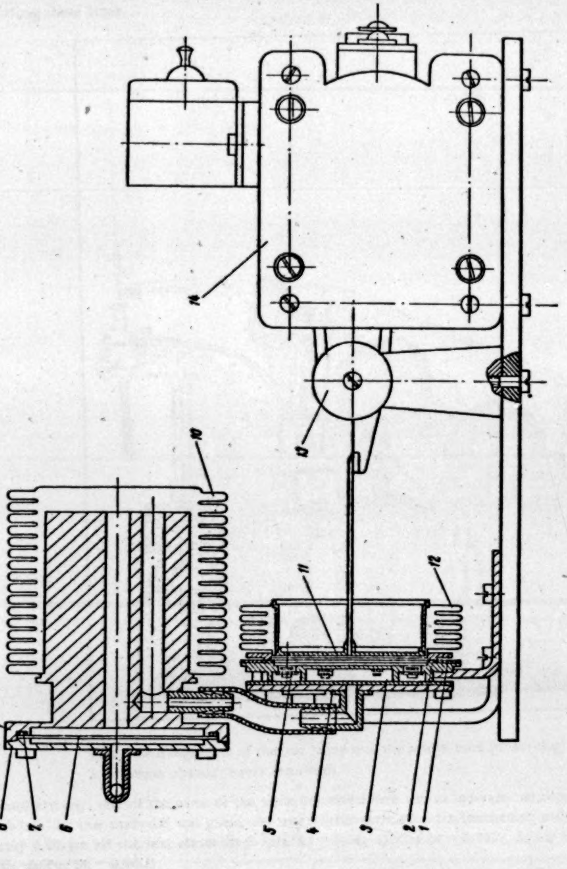

Fig. 3. Diagram of the pump.

In the chambers 3 and 5 of the pump head 2 are fitted valves made from fine, elastic foil. The gas passes from the pump into a reservoir, in which, as the result of the elasticity of the belows 10, pressure pulsations are smoothed out.

The filter layer 6 ensures complete freedom of the gas from accidental contamination. The gas feeding chamber 5 of the pump passes into the same reservoir, thereby ensuring smoothing out pulsations in the intake branch of the system. The comparative simplicity of construction, and the absence of friction in the chief points ensure continuous and stable pump operation.

All the parts serving the arc lamp, as well as the fittings used for directing and controlling the various operations, can be fitted into an apparatus which can be set up on the spectrograph track. Fig. 4 gives an idea of the first attempt along these lines.

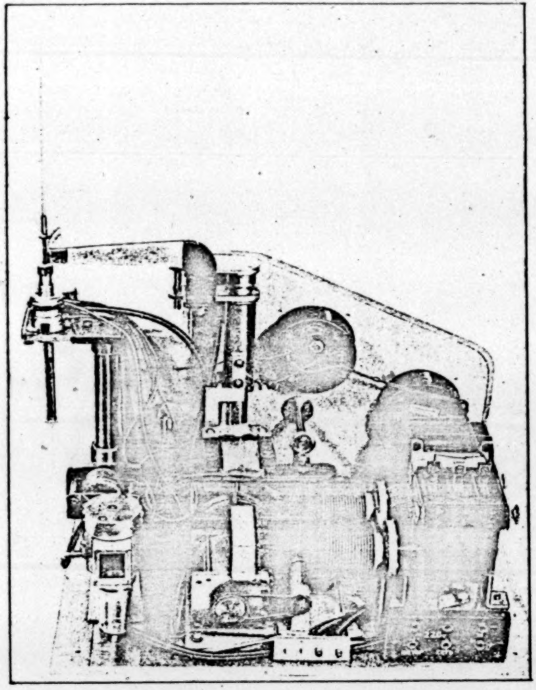

Fig. 4. Arrangement of the arc lamp and the setups used for serving it on a common chassis (cover removed).

As noted already, one of the aims of the work described here was to increase the reproducibility of an arc discharge. When the test material was glass, the mean arithmetic error for blackening differences proved to be approximately 0.01 for all the test elements ($\Delta SNa/Li - 0.01$; $\Delta SCa/Sn - 0.012$; $\Delta SAl/Sn - 0.013$; $\Delta SMg/Sn - 0.008$; $\Delta SFe/Sn - 0.009$).

Thus by taking several photographs of the spectrum for each sample it is possible to work with a relative error not exceeding 2 %. It is possible to determine all oxides from the general spectra. The slopes of the calibration curves for various elements practically coincide with each other.

It remains to point out that the arc lamp is of general application, and by means of it evaporation of a considerable number of various materials can be realized, the same techniques being used in each case.

SUMMARY

An arc lamp has been developed for the spectrographic analysis of powders in a dc carbon arc; use is made of the following techniques: a) a protective atmosphere is used which protects the electrodes from rapid wear; b) the test material is fed continuously into the discharge through an anode canal; c) a permanent self-sharpening upper electrode is used; d) the amount of inert gas used is cut down by using the same gas repeatedly after it has been purified in a special filter; e) the discharge is blown along the periphery by gas whose circulation is ensured by a pump; f) dismantling and subsequent assembling of the apparatus for changing samples and electrodes can be carried out rapidly.

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DETERMINATION OF GALLIUM IN MINERALS BY MEANS OF THE RHODAMINE PHOTOMETRIC METHOD

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The main disadvantage of reactions on which methods of determining small amounts of gallium [1 - 5] are based is their low selectivity. Separation of gallium is carried out by multiple extraction from hydrochloric acid solutions of its chloride by means of ether [1-4], or amyl acetate [5], and this complicates work considerably when carrying out mass analyses.

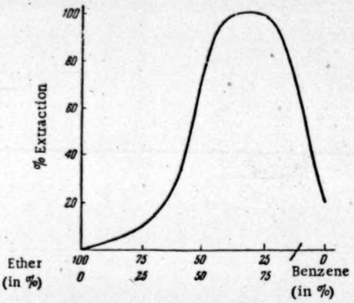
We have improved the photometric method for the quantitative determination of gallium by using rhodamine B, which was suggested by Onishi and Sandell[3], in such a way, that the operation involving preliminary separation of gallium from accompanying elements can be omitted. Gallium can be determined in minerals independently of the iron and aluminum contents of the minerals. When gallium ions interact with rhodamine B in 6 N HCl, colored rhodamine chlorogallate is formed which is extracted with benzene. The presence of upwards of 0.5 γ of gallium can be detected by the appearance of a red-violet color in the organic layer, below 0.5 γ the presence of gallium is shown by the appearance of an orange-yellow fluorescence. Interference on the part of Au^{III}, Fe^{III}, Sb^{V} and Tl^{III} can be eliminated by addition of titanium trichloride to the original solution; other foreign ions, with the exception of NO_3^+, do not interfere with the detection and determination of gallium.

Quantitative determination of gallium by Onishi's method [6] (without preliminary extraction) is hindered by the low value of the extraction coefficient of rhodamine B chlorogallate by benzene, and its dependance on the composition and concentration of impurities in solution. We established that a mixture of ether and benzene has a greater capacity for extracting the rhodamine B complex of gallium from its hydrochloric acid solution, than either benzene or ether alone.

The extraction curve for rhodamine B chlorogallate from 6 N HCl (diagram) exhibits a clearly defined maximum corresponding to 100% transfer of the complex into the organic layer, at a volume ratio of ether to benzene of 1 : 3. Percentage extraction of the rhodamine complex of gallium by a mixture of 1 volume of ether and 3 volumes of benzene is practically independent of the content of impurities. The extraction action of the ether-benzene mixture on rhodamine B chlorogallate, is, presumably, similar to the dissolving of a solid material in a mixture of liquids, which when taken separately, do not dissolve this material at all. Thus, Grinberg and Sul'man [7] found that the salt $[Pt(NH_3)_4][Pt(SCN)_4]$ while practically insoluble in water and in dry acetone, readily dissolves in aqueous acetone, and the value of the solubility at a given temperature depends on the ratio between the amounts of acetone and water. Maximum solubility is observed at a content of 61.7 % of acetone in the system acetone-water. This phenomenon has been explained by the presence of affiliated solvation, i.e. by a type of solvation in which one part of the complex molecule of the compound to be dissolved is preferentially solvated by one of the mixed solvents, while the other part of the molecule is solvated by the other component of the mixed solvents, and the sum of the partial energies of solvation of the separate components of the given compound exceeds the energy of the crystalline lattice, as a consequence of which the salt dissolves.

The use of a benzene-ether mixture for extracting the rhodamine complex of gallium permits visual colorimetric determination for gallium content in the test material of 0.2 to 1 γ with an accuracy of 0.1 γ; from 1 to 2 γ with an accuracy of 0.3 γ; from 2 to 5 γ with an accuracy of 0.5 γ, and from 5 to 10 γ with an accuracy of

1 γ. The relative error of such determinations amounts to 10-15 % on an average. The minimum amount of gallium which can be detected on the basis of the color of the benzene-ether layer is equal to 0.1 γ/ ml.



Curve illustrating extraction of rhodamine B chlorogallate by a mixture of ether and benzene (the composition of the mixture is given in volume %).

The method developed has been tried out on more than 200 samples of gallium-containing minerals; bauxites, natrolites, nephelines, sphalerites, pyrite-gallenites, etc. The minimum content of gallium which can be determined by means of the rhodamine method, without resorting to preliminary separation of gallium from accompanying elements, amounts to (in the case of sulfide ores, natrolites, and nephelites) ten thousandths of a percent, and in the case of bauxites and certain silicates, thousandths of a percent.

Results on gallium content of minerals, which were obtained by means of the rhodamine method, were compared with results obtained by the method of Lukin and coworkers [5], and also with the results of measurements also carried out by the same rhodamine method, but with the inclusion of the operation of carrying out a preliminary separation of gallium from other elements (Table). Gallium is separated from the other elements by extraction of its chloride with ether [3]. As the results in the table show, the extent of the deviation of the results does not exceed the experimental error which is 10-15 %.

Determination of Gallium in Minerals

Mineral		Chief accompanying elements	Gallium found, in %		
			rhodamine method– no removal of impurities present	rhodamine method with prior removal of gallium chloride	by Lukin's method with gallion
Natrolite	$Na_2[Al_2Si_3O_{10}]2H_2O$	Fe, K	0.02	0.02	0.02
Nepheline	$Na[AlSiO_4]$	Fe, Ca, K	0.01	0.01	0.01
Bauxite	$Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.006	0.0055	0.006
"	$Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.006	0.006	Fe interferes
"	$Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.002	0.002	"
"	$Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.01	0.009	"
"	$Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.005	0.005	0.0045
Sphalerite	ZnS	Si, Pb. Cu, Fe. Cd	0.06	0.06	Fe interferes
"	ZnS	Si, Pb. Cu, Fe. Cd	0.027	0.03	"
"	ZnS	Si, Pb. Cu, Fe. Cd	0.04	0.042	"
"	ZnS	Si, Pb. Cu. Fe. Cd	0.025	0.026	"

ANALYTICAL PROCEDURE

A sample of bauxite or silicate (0.25 g) is fused with 1 g Na_2CO_3 for 10 minutes at 1000°. Large amounts of sodium carbonate are not recommended. The melt is leached and neutralized with excess hydrochloric acid, the mixture is then evaporated on a water bath to dryness, the residue is moistened with 5 drops of concentrated HCl and dissolved in 25 ml of water, the solution is transferred to a 50 ml standard flask and its volume made up to the mark with hydrochloric acid,sp.gr. 1.19. When these instructions are followed the solution obtained will be 6 N with respect to HCl. After standing, or after the solution has been filtered through a dry filter, 2 ml of the transparent solution is transferred to a colorimeter tube.

Sulfide minerals (sphalerites, gallenites, pyrites, and chalcopyrites) are dissolved in a different way. An aliquot of the mineral (0.1-1 g) is placed in a 50 ml beaker and dissolved by boiling in concentrated HCl (10-15 ml) and adding hydrogen peroxide dropwise. The solution is evaporated to dryness on a water bath, and the residue dissolved in 6 N hydrochloric acid. The solution is transferred to a 25 ml standard flask. 2 ml of this solution is taken for further work.

During analysis of pure sphalerites and gallenites, 0.1-1 g of the mineral is boiled under a funnel in a 50 ml conical flask with 17-20 ml of 6 N hydrochloric acid for 5-10 minutes. The transparent, cold solution is transferred to a 25 ml standard flask, the conical flask being rinsed out with 6 N HCl, and the solution is then made up to the mark with 6 N HCl.

A standard color scale is prepared by transferring a gallium solution which is 6 N with respect to HCl into colorimeter tubes with ground glass stoppers, in amounts containing 0.2, 0.3, 0.6, 1, 2 and so on through 10 γ of gallium. The volume of each solution is made up to 2 ml with 6 N HCl. To these solutions, and also to the standard solution, is added 0.5 ml of 20 $TiCl_3$ solution and 1 ml of HCl sp.gr. 1.19, and after 5 minutes, 0.4 ml of rhodamine B is added (0.5 % in 6 N HCl), and the whole thoroughly mixed.

For iron contents greater than 200 mg/ ml, 1 ml of the solution of test material, 1 ml of 20 % $TiCl_3$ solution, and 1 ml of HCl sp. gr. 1.19 should be taken. The amount of rhodamine B remains the same as before (0.4 ml).

1.5 ml of benzene and 0.5 ml of ether are added to each tube to extract the gallium complex. The tube and its contents are shaken for 1.5-2 minutes, and, after separation of the aqueous and organic layer (5-10 minutes), the color of the benzene-ether layer of standard and test solutions is compared in transmitted light.

The standard solution is prepared by treating 0.1 g of gallium metal with 10 ml of aqua regia in a conical flask under a funnel, gentle heat being used. The solution obtained is evaporated to dryness. In order to remove traces of HNO_3, the residue is evaporated twice with HCl, and then transferred by means of 6 N HCl to a 100 ml standard flask. The solution obtained is diluted with 6 N hydrochloric acid. A suitable concentration for work is 10 γ of gallium per ml.

SUMMARY

A photometric method has been developed for the determination of small amounts of gallium, in which rhodamine B chlorogallate is extracted with a mixture of 1 volume of ether and 3 volumes of benzene.

By means of this method it is possible to determine 0.0001-0.1 % of gallium in bauxites, silicates, sphalerites, pyrites, gallenites, and other gallium-containing minerals, with an error of 10-15 %, without separating the gallium from accompanying elements.

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A NEW REAGENT FOR THE PHOTOMETRIC DETERMINATION OF GALLIUM — GALLION

COMMUNICATION I. THE EFFECT OF SUBSTITUENTS ON THE PROPERTIES OF ORGANIC REAGENTS

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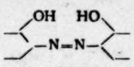
Information on the effect of substituents* on the analytical properties of various organic reagents used for determination of cations is very plentiful (see for example [1-33] etc.). All the same this question has not been studied sufficiently in the case of series of azo compounds. The objects of the present study were mono azo dyes containing the o,o'-dihydroxyazo group [I] as the characteristic (functional-analytical) group. Of the numerous representatives of this series of compounds, we settled on those which were obtained by coupling diazo compounds obtained from o-aminophenol and its derivatives with β-naphthol and its sulfonic acids, with chromotropic and H-acids, and with a series of other azo compounds. In the present article we shall deal only with results obtained in the case of compounds formed by coupling (in alkaline media) with H-acid. The substituents used were NO_2, HSO_3, and Cl. For this work we chose only those mono- and disubstituted o-aminophenols (Table 1) which contained the substituents indicated, in the ortho- and para positions with respect to the hydroxyl group (in formula (II) these places are denoted by asterisks).**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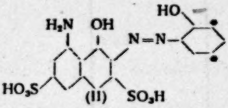

(II)

Coupling of the diazo compounds obtained from the listed substituted o-aminophenols and from o-aminophenol itself, with H-acid in a sodium carbonate medium did not lead to any special difficulties; many of the dyes which were synthesized have already been described, accordingly, we shall not dwell on their synthesis. All the azo compounds were prepared in a chemically pure state by various techniques.

Compound (II) is in itself of no great interest as a reagent. All the same, we turned our attention to the fact that aqueous solutions of this compound in an acid medium change color appreciably in interacting with 50 γ gallium (from a raspberry color to a reddish-violet color) (Table 1). On these grounds we decided to investigate the effect of substituents in a series of derivatives of compound (II), and to concentrate mainly on their interaction with gallium, particularly since only few sensitive color reactions are known for gallium [34-39].

Results obtained during the study of all the materials synthesized are collected together in Table 1. The

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* By the term "substituent" we mean any group or atom introduced into the molecule of the original reagent by substitution of a hydrogen atom in its skeleton, irrespective of their arrangement, and the nature of their participation in interactions with certain cations.

** These substituted o-aminophenols were kindly placed at our disposal by I. I. Vorontsov, to whom we extend our sincere thanks.

TABLE 1

Characteristics of the Color Reactions which Occur During Interaction of Azo Dyes Obtained from H-Acid with Gallium

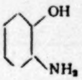
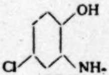
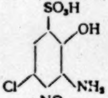
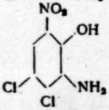
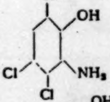
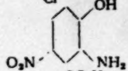
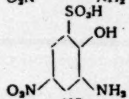
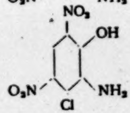
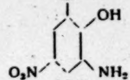
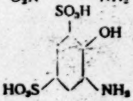
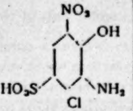
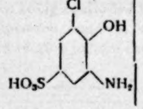
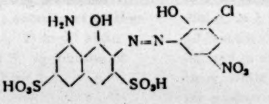
Number of test	Diazo component	Contrast of color reactions with 50 γ gallium		Sensitivity in γ Ga	Characteristic of the scale from 0.5 to 6 γ Ga
		Color solution without Ga	Color solution containing Ga	In 5 ml	
1.		Raspberry	Reddish-violet	1	Poor (little contrast)
2.		•	Violet	1–1.5	No scale
3.		•	Blue-violet	0.5	Worse than in Nos. 7 and 9
4.		•	Blue	•	Poor
5.		•	Raspberry	—	—
6.		•	Violet-blue	1.5	No scale
7.		•	Blue	0.5	Good
8.		•	Light blue	2	Poor
9.		•	Blue	0.2	Good
10.		•	Violet-blue	1	Poor

TABLE 1 (continued)

Number of test	Diazo component	Contrast of color reactions with 50 γ gallium		Sensitivity, in γ Ga	Characteristic of the scale from 0.5 to 6 γ Ga
		Color solution without Ga	Color solution containing Ga	in 5 ml	
11.		Orange-raspberry	Blue	0.75–1	Poor
12.		Raspberry	Violet-blue	0.5	Worse than in Nos. 7 and 9

experiments were carried out in a mixture of solutions of acetic acid and urotropine (pH about 3.5). (Later [41] a more efficient buffer mixture was found). The color achieves its maximum at room temperature after 4-5 minutes, while at 98-100° maximum color is reached in 1 minute.

Analysis of the results obtained shows that, in particular: 1) the nature, number, and position of the substituents introduced have an essential effect on the analytical properties of the derivative; 2) a nitro group in the ortho position with respect to the hydroxyl group exhibits a negative influence on the analytical properties; 3) the compounds shown in Nos. 3, 7, 9, and 12 are the most interesting as reagents for gallium, since they have the highest sensitivity for this element, there being little difference between the sensitivities of these four compounds, further, they give a scale which exhibits sufficient contrast, although the scale differs from one to the other; 4) of these four compounds, two (Nos. 7 and 9) possess the greatest interest from the point of view of the photometric determination of gallium, particularly with respect to scale contrast; in turn, of these two compounds — 7 and 9 — particularly in view of differences in scale contrast, we gave preference to No. 9, whose solutions showed a somewhat greater stability than those of No. 7. G. G. Karanovich [41] has confirmed that compound No. 9 does actually have some advantage over compound No. 7, and is of undoubted interest for the photometric determination of gallium (particularly in the case of certain rocks). This compound, i.e. 2-hydroxy-3-chloro-5-nitrobenzene-(1-azo-2')-1'-hydroxy-8'-aminonaphthalene-3',6'disulfonic acid is called "gallion"* (III).



Thus, the present work has shown that, in certain cases, substituents may have considerably greater influence than might have been expected on the basis of published results [31, 42, 43, 44, 45].

We have an example therefore in the present work of a case where a compound which does not possess valuable analytical properties, and which, accordingly is of no practical importance, being converted into a fairly valuable reagent by the introduction of substituent. It is worth pointing out that we chose as objects of our research compounds containing the reacting group (I) whose "nonspecificity — according to published results — should prevent the wide application of ortho-hydroxy azo compounds as analytical reagents" [46]. It is precisely in this series of compounds that the introduction of a substituent leads to the creation of a reagent for gallium. Finally, the results which we have obtained do not demonstrate any new principle. All that we have done is to extend the results of investigations into the effect of substituents to materials which have not been studied previously.

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* This is issued by the chemical industry under the name "Gallion IREA."

Hitherto, the best reagent, of the large number of reagents which have been described in the literature [34-40 and 47-57] for the photometric determination of gallium, has been quinalizarin [36, 37]. Comparison of the new reagent with quinalizarin has also been carried out by G. G. Karanovich [41] who demonstrated the advantages of gallion over quinalizarin.

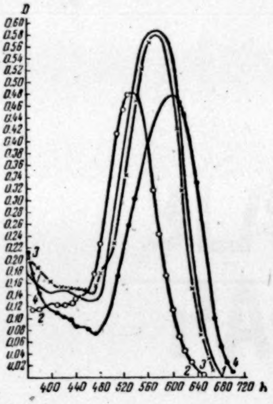
SYNTHESIS OF GALLION[*]

We were unable to find a description of the synthesis of gallion.

1.88 g of 2-amino-4-nitro-6-chlorophenol, which had been recrystallized from water, and had a melting point of 163-164°, was added to a mixture of 1.5 ml of concentrated hydrochloric acid and 15 ml of water. The suspension obtained was diazotized at room temperature by addition of a solution of 0.7 g of sodium nitrite in 5 ml of water, the reaction being controlled in the usual manner. The diazo compound, which was obtained in the form of a straw yellow suspension, was kept for 10 minutes, and then added to a solution of 3.9 g of H-acid (the monosodium salt) in 30 ml of 10% sodium carbonate; as the diazo compound was added, the reaction mass acquired a brownish-violet color and thickened considerably as the result of the formation of a precipitate of the reaction product. 3 hours after coupling, the black-violet reaction mass was filtered, the precipitate was then reprecipitated twice by dissolving in water on heating, and then acidifying. The first time the precipitate was dissolved in 140 ml water and the solution filtered while still hot from possible insoluble impurities, the hot violet filtrate was acidified with concentrated hydrochloric acid until the solution gave an acid reaction to Congo paper. The second time, the bright red precipitate formed was dissolved in 200 ml of boiling water, and the red solution obtained was acidified with 40 ml of concentrated hydrochloric acid. The precipitate was again filtered off and dried (for analysis, at 160-170°). 3.5 g of reagent was obtained. The preparation obtained was practically free from sodium.

Found %: S 12.34; 12.55; Cl 6.83; 6.93.
$C_{16}H_{11}O_{10}N_4S_2Cl$. Calculated %: S 12.36; Cl 6.83.

The product obtained is a brick-red, fine, crystalline powder; its aqueous solutions have a bluish-raspberry color, in 1 % hydrochloric acid the color of this solution is bluish-violet, in 1 % sodium hydroxide the color is violet, in 10 % sodium carbonate the color is bluish-violet, in ethanol and in concentrated sulfuric acid the color is raspberry, while in acetone, benzene, and carbon tetrachloride the product is practically insoluble.



Absorption curves for 0.001 % aqueous solutions of gallion: 1) solution of gallion in water (pH about 4.0); 2) at pH about 2.5; 3) at pH about 11.5; 4) solution of gallion + Ga^{3+} at pH about 2.2.

Absorption curves[**] for aqueous solutions of the reagent at three pH values, and for a solution of its interaction product with gallium are given on the diagram.

SUMMARY

A study of the effect of substituents on the analytical properties of a series of azo dyes has shown that, while the product obtained by coupling H-acid in an alkaline medium with a diazo compound derived from o-aminophenol has no analytical value, some of its substituted derivatives are suitable (from the point of view of sensitivity, contrast, color stability, and other properties) for the photometric determination of gallium; of these substituted derivatives it has been found that the most valuable as a reagent for gallium is the product obtained by coup-

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[*] N. S. Simonova took part in the synthesis.

[**] Taken by Iu. I. Pecherskaia at IREA on an SF-4 spectrophotometer.

ling H-acid with the diazo compound obtained from 2-amino-4-nitro-6 chlorophenol; this compound which has been called "gallion" is 2-hydroxy-3-chloro-5-nitrobenzene-(1-azo-2')-1'-hydroxy-8'-amino-naphthalene-3',6'-disulfonic acid.

By the introduction of a substituent in the case studied, changes in analytical properties have been achieved, as compared with the original unsubstituted compound which is of no practical value, such that, even in the case of a reacting group with low specificity, the original compound has been transformed into a valuable reagent.

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* In Russian.

** Original Russian pagination. See C. B. Translation.

PHOTOMETRIC DETERMINATION OF TANTALUM IN TITANIUM AND ITS ALLOYS BY MEANS OF ARSENAZO REAGENT

E. I. Nikitina

During determination of tantalum and niobium in various materials, the most difficult problem is their separation from titanium. Titanium, as a rule, reacts with the same reagents as the metals mentioned. During precipitation by acid hydrolysis, precipitation with phenylarsonic acid, tannin, and pyrogallol, titanium is always coprecipitated with tantalum and niobium, and this requires repeated reprecipitation in order to free these metals from titanium salts [1-2]; even then it is still necessary to correct for trapped titanium in the final result. Determination of tantalum in titanium alloys is made even more difficult as the result of the unfavorable ratio of tantalum to titanium. During precipitation of tantalic acid in titanium alloys by acid hydrolysis, or by hydrolysis with pyrogallol or phenylarsonic acid and other materials, low results are obtained for tantalum.

Titanium also interferes with the photometric determination of tantalum by means of pyrogallic acid [2], and tantalum must be separated beforehand.

The present article contains a description of a method for the photocolorimetric determination of tantalum in titanium alloys, on a background of titanium, by means of the reagent arsenazo, in which there is no need to carry out a preliminary separation of tantalum.

The Color Reaction of Tantalum with Arsenazo. Arsenazo, or benzene-2-arsonic acid <1-azo-7> 1,8-dihydroxynaphthalene-3,6-disulfonic acid, has been recommended as a reagent for the photometric determination of the rare-earths [3], quadrivalent vanadium [4], zirconium [5], aluminum [6], and niobium.*

Tantalum compounds form colored compounds with colored organic reagents of the type R—OH in acid solutions.

Pyrogallol [2], aluminon**, and arsenazo [3] also, are organic reagents of this type.

Arsenazo has a rose color in netural and acid aqueous solutions; in the presence of tantalum, as in the case of niobium, the color changes to violet.

The color reaction between tantalum and arsenazo to form a colored complex only occurs in strongly acid media at pH 2. The colored soluble complex between arsenazo and tantalum is formed at room temperature immediately on addition of arsenazo to the acid solution of tantalum.

In contrast to the color reaction of tantalum with aluminon, tantalum forms a colored compound with arsenazo both in an acetic acid medium at pH 2 and in hydrochloric and sulfuric acid media at $pH < 2$. In such cases, where the solutions contain hydrochloric acid, no hydrolysis of the tantalic acid is observed in the presence of arsenazo on long standing (for 48 hours).

The maximum color intensity of the complex in solutions containing acetic or hydrochloric acid (Table 1) is observed at pH 1-2.

The color of the tantalum complex with arsenazo is stable, readily reproducible, and completely suitable for colorimetric determination of tantalum, when hydrochloric acid solutions are used.

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* Developed by V. I. Kuznetsov and S. I. Barskaia.

** E. I. Nikitina.(In press).

An increase in the acidity of the solution within the limits of 0.1 to 2 N with respect to hydrochloric acid does not hinder formation of the colored complex of tantalum with arsenazo; the optical density of the solution remains practically constant for 0.03-1 mg of tantalum. For tantalum contents of 0.03 to 1 mg, the reaction between the intensity of the colored complex of tantalum with arsenazo and its concentration is linear (Fig. 1).

TABLE 1

Relation between Optical Density and Nature of the Acid

Tantalum taken, in mg	Optical density in the medium		
	CH_3COOH pH 2	HCl pH 1	H_2SO_4 pH 1
0.14	0.24	0.23	0.18
0.28	0.36	0.35	0.26

The reaction between tantalum and arsenazo is much more sensitive than the reaction of this metal with pyrogallol; by means of the reaction with arsenazo it is possible, as in the case with aluminon, to determine 0.3 γ/ml of tantalum. Tantalum only forms a colored soluble compound with arsenazo in strongly acid solutions, consequently it is not essential to convert tantalum pentoxide into soluble potassium tantalate by fusing it with potassium carbonate.

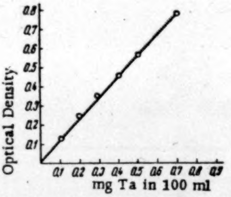

Fig. 1. Relation between the color of the tantalum-arsenazo complex and tantalum concentration, in the absence of complexing agents.

Since there are no simple compounds of tantalum and niobium which are soluble in aqueous media, it is possible, in order to get the colored compound with arsenazo, to start from solutions of potassium tantalate in potassium carbonate, as indicated in [3]. Addition of a solution of arsenazo to a weak alkali solution of potassium tantalate prevents deposition of tantalic acid during subsequent addition of hydrochloric acid; in the presence of arsenazo, during neutralization with hydrochloric acid, the soluble complex of tantalum with arsenazo is immediately formed.

When acid tartrate or citrate solutions of tantalum (see below) are used, the colored compound is formed on addition of arsenazo to a solution containing hydrochloric acid at pH ≤ 1.

Photometric determination of tantalum with arsenazo is best carried out on the basis of the mixed color obtained from excess reagent and the violet color of the tantalum complex. The mixed color is obtained on adding 5 ml of a 0.05% solution of the reagent to solutions containing from 0.2 to 2 mg of tantalum in 100 ml solution.

TABLE 2

Determination of Tantalum with Arsenazo

Tantalum taken, in mg	Tantalum found, in mg	Tantalum taken, in mg	Tantalum found, in mg
0.03	0.038-0.036	0.30	0.32-0.33
0.056	0.06-0.06	0.56	0.54-0.56
0.112	0.10-0.10	0.70	0.68-0.70
0.14	0.15-0.15	1.12	1.10-1.0
0.20	0.21-0.23	1.40	1.45-1.50

On Fig. 2 are shown light absorption curves for solutions of the complex formed between tantalum and the reagent. Maximum light absorption of the tantalum complex in hydrochloric acid solutions is observed at 580 mμ when using a yellow orange filter. In this spectral region, the solution of pure arsenazo exhibits minimum light absorption. The color intensity of the tantalum complex with arsenazo was measured by means of an FEK-N photocolorimeter with a No. 6 light filter. Table 2 contains the results of photocolorimetric determinations carried out by means of arsenazo on amounts of tantalum ranging from 0.03 to 1.4 mg in hydrochloric acid media.

The values given in Table 2 show that the results obtained during photocolorimetric determination of tantalum with arsenazo exhibit good reproducibility.

Influence of Complexing Agents on the Reaction of Tantalum with Arsenazo. Various complexing agents present in solution exhibit different effects on the reaction of tantalum with arsenazo. The oxalate and fluoride complexes of tantalum are more stable than the complex of the latter with arsenazo at room temperatures; in the presence of these complexes,therefore, that with arsenazo is not formed. Nevertheless, on heating the solution to 100°, the oxalate complex of tantalum partially breaks down, and, on addition of arsenazo under these conditions, the color of the complex formed between tantalum and arsenazo appears (Table 3).

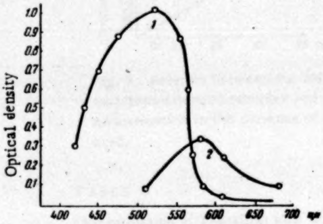

Fig. 2. Light absorption curves of solutions of the complex of tantalum and arsenazo: 1) reagent; 2) tantalum complex.

The tartrate and citrate complexes of tantalum are less stable in acid solutions than the oxalate and fluoride complexes, and also less stable than the arsenazo complex.

Tartrate and citrate solutions of tantalum, containing 5 ml of arsenazo solution break down completely at room temperature, and more rapidly at 100°; under these conditions, the color of the tantalum compound with arsenazo develops quantitatively in hydrochloric acid media (Table 3).

As the results given in Table 3 show, determination of tantalum can be carried out from its tartrate and citrate solutions, without resorting to preliminary conversion of tantalic acid into potassium tantalate.

The relationship between the intensity of the color and tantalum concentration in a solution containing tartrate is shown in Fig. 3. In the range 0.03 to 0.8 mg of tantalum, the intensity of the color of the complex conforms to the Lambert – Beer law.

TABLE 3

Development of the Color of the Tantalum Complex with Arsenazo in the Presence of Masking Agents

Complexing agent	Concentration, in g/ml	Tantalum taken, in mg	Optical density of the complex with arsenazo	
			At 20°	At 100°
Hydrofluoric acid		0.14	0	0
	0.0002	0.28	0	0
Oxalic acid	0.01	0.14	0	0.07
		0.28	0	0.14
Tartaric acid	0.02	0.14	0.05	0.09
		0.28	0.18	0.21
Citric acid	0.02	0.14	0.07	0.11
		0.28	0.21	0.24

During photometric determination of tantalum by means of arsenazo in a solution containing tartrate, the concentration of free tartaric acid is of great importance. The presence of tartaric acid depresses the color intensity of the complex of tantalum with arsenazo (Figs. 1, 3), and in the case of a large excess of tartaric acid, the solution may be completely decolorized. The lower the content of free tartaric acid in solution, the more intense the color of the tantalum complex. During quantitative determination of tantalum with arsenazo in solutions containing tartrate, it is essential to keep the concentration of tartaric acid constant.

In the experiments described below (Table 4) on the photocolorimetric determination of tantalum, and also for the construction of a calibration curve (Fig. 3), 10 ml of a 20 % solution of tartaric acid per 100 ml of solution was used.

Table 4 contains results obtained during the photocolorimetric determination of tantalum by means of arsenazo.

Table 4 shows that the results exhibit good reproducibility.

Experimental Procedure. 0.05 g of pure tantalum oxide was fused with 3 g of potassium pyrosulfate and the melt leached with 20 ml of 20 % tartaric acid and 20 ml of water. The solution was transferred to a 200 ml standard flask and made up to the mark with water. An aliquot of solution containing from 0.03 to 1.0 mg of tantalum was pipetted into another standard flask with a capacity of 100 ml, 15 ml of water, 5 ml of a 0.05 % solution of arsenazo, and 20 ml of hydrochloric acid 1 : 1 were then added. This solution was heated to the boil, then cooled, and made up to the mark with water, color intensity was measured with a yellow-orange filter (No. 6 FEK-N) using a 50 mm cell. The tantalum content was found by means of a calibration curve constructed under the same conditions.

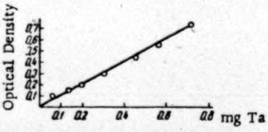

Fig. 3. Relation between the color of the tantalum-arsenazo complex and tantalum concentration in the presence of tartaric acid.

TABLE 4

Determination of Tantalum with Arsenazo in Solutions Containing Tartrate

Tantalum taken, in mg	Tantalum found, in mg
0.04	0.035
0.08	0.085
0.16	0.15
0.26	0.27
0.35	0.36
0.40	0.39
0.70	0.72
0.84	0.86
1.12	1.12

The Effect of Titanium on the Formation of the Tantalum-Arsenazo Complex. Titanium at room temperature gives a violet color with arsenazo in hydrochloric, sulfuric, and tartaric acid solutions with pH 2. Tests showed that on increasing the acidity of the solution to pH 0.5, at room temperature, and even more rapidly at 100°, the color of the titanium complex with arsenazo is completely destroyed.

On Fig. 4 are given light absorption curves for solutions of the complex formed between titanium and reagent at various pH values. It follows that at pH< 0.5, titanium will not interfere with determination of tantalum by means of arsenazo. Actually, in a medium of 1 N hydrochloric acid, and on heating to 100°, the complex of tantalum with arsenazo is formed quantitatively in the presence of titanium, the titanium complex being decolorized under these conditions. In amounts of 5 to 20 mg, titanium, in strongly acid solutions, does not interfere with the formation of the colored tantalum-arsenazo complex, but, it does, nevertheless, depress the color intensity insignificantly. Consequently, it is best to construct a calibration curve in the presence of 5-10 mg titanium. When titanium is present in amounts in excess of 20 mg, it is essential to alter the conditions of the photometric determination by increasing the acidity of the solution. The relationship between the color intensity of the tantalum-arsenazo complex and its concentration, in the presence of 5-10 mg titanium, is shown on Fig. 5. Under these conditions, the color intensity of the tantalum-arsenazo complex is proportional to its concentration for amounts of tantalum ranging from 0.05 to 0.8 mg.

Table 5 contains the results for the photocolorimetric determination of tantalum in the presence of titanium by means of arsenazo.

To a solution of 0.01 g of titanium in sulfuric and tartaric acids was added varying amounts of a tartaric solution of tantalum, and the tantalum determined photocolorimetrically by means of arsenazo. The tantalum content was determined by means of the calibration curve which had been constructed by means of a standard tantalum solution in the presence of 0.01 g titanium.

TABLE 5

Determination of Tantalum in the Presence of Titanium
(0.01 g Ti taken)

Tantalum taken, in mg	Tantalum found, in mg
0.14	0.13-0.12
0.28	0.26-0.27
0.32	0.31-0.32
0.56	0.56-0.58
0.84	0.81-0.82
1.10	1.07-1.08

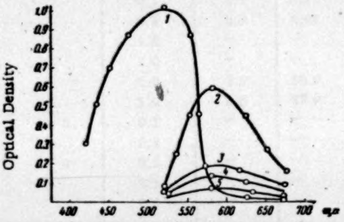

Fig. 4. Light absorption curves of solutions of the titanium-arsenazo complex at various pH values, for equal amounts of reagent and titanium:
1) reagent; 2, 3, 4, 5) titanium-arsenazo complex at pH 3-2, 1, 3; 1 and 0.5.

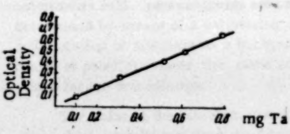

Fig. 5. Relation between the color of the tantalum-arsenazo complex and tantalum concentration in the presence of 10 mg titanium.

The values given in Table 5 demonstrate the good reproducibility of the results. Under the conditions described above, titanium does not interfere with the photocolorimetric determination of tantalum by means of arsenazo in tantalum tartrate compounds.

Experiments were next carried out on direct determination of tantalum in titanium alloys, without removal of titanium. Sulfuric acid was used in our experiments, to avoid hydrolysis of tantalic acid during dissolving of the titanium alloys. The titanium alloys dissolved readily in sulfuric acid, and, at sulfuric acid concentrations of 1 : 1, no hydrolysis was observed for contents below 8 % of tantalic acid in the alloy.

Nitric acid and ammonium persulfate were used for oxidizing trivalent titanium when the alloys were dissolved in acid. In the presence of nitric acid, on subsequent addition of arsenazo solution, the color of the tantalum complex did not develop completely and low results were obtained. Ammonium persulfate not only oxidizes trivalent titanium, but also prevents polymerization of tantalic acid in the sulfuric acid solution, thereby favoring transformation of the complex polymerized particles into true solutions or into solutions containing low polymer compounds. When titanium alloys containing more than 8 % tantalum were dissolved in sulfuric acid, tantalic acid was precipitated. Addition of a solution of ammonium persulfate, with subsequent heating of the turbid solutions, favors depolymerization, i.e., complete dissolution of the precipitated tantalic acid. In all subsequent work titanium alloys were dissolved in sulfuric acid with subsequent oxidation by ammonium persulfate, the tantalic acid is thereby kept completely in solution. The precipitated tantalic acid can also be dissolved by evaporating the solutions to the appearance of white fumes of sulfuric acid.

As soon as the conditions had been found for getting tantalic acid into solution quantitatively during the dissolving of titanium alloys, experiments were carried out on the photocolorimetric determination of tantalum in titanium alloys on a background of titanium, in sulfuric acid solutions containing tartrate. Results of these experiments are given in Table 6.

The results given in Table 6 show that the main bulk of the titanium does not interfere with determination of tantalum by means of arsenazo. Determination of tantalum by means of arsenazo using the conditions just described is simple to carry out, and can be carried out on a background of titanium without preliminary separation of the latter.

Effect of Other Cations. The presence in titanium alloys of aluminum in amounts up to 10 %, and of iron in amounts up to 1.0 % does not interfere with tantalum determination by means of arsenazo. Iron in amounts greater than 1.0 % depresses the color intensity of the tantalum-arsenazo complex, and, at iron contents of 20 to 100 mg, the tantalum-arsenazo complex is not formed. The alkali and alkaline-earth metals do not interfere with tantalum determination. Zirconium in amounts less than 1.0 mg in the solution taken for photometric measurements does not interfere with tantalum determination.

TABLE 6

Photocolorimetric Determination of Tantalum in Titanium Alloys

Alloy	Titanium aliquot, in g	Tantalum added, in mg	Tantalum found, in mg	Tantalum found (in %) after subtracting the amount added
1	0.1	2.8	2.9	
	0.1	1.4	1.45	
	0.1	0.7	0.8	
	0.1	0.2	0.25	
2	0.1	–	–	2.1
	0.1	–	–	2.14
	0.1	1.4	3.52	2.12
	0.1	2.8	4.84	2.04
	1.0	–	–	2.0
	1.0	–	–	2.0
	1.0	5.6	26.0	2.04
	1.0	5.6	27.0	2.12
3	0.1	–	–	8.1
	0.1	–	–	8.2
4	0.1	–	–	12.5
	0.1	–	–	12.7
	0.1	–	–	12.8

Since niobium is similar to tantalum in its chemical properties, and since it also forms a complex with arsenazo [3], it was necessary to establish the behavior of niobium toward arsenazo in the presence of tartaric acid. Tests showed that the tartrate complex of niobium, under the conditions used for tantalum determination, also forms a stable, violet colored, soluble complex with arsenazo. The sensitivity is the same as in the case of tantalum (0.3 γ/ml). Titanium does not interfere with formation of the niobium-arsenazo complex. Consequently, when niobium is present as well as tantalum in the titanium alloys, total tantalum and niobium is determined. Niobium interferes with determination of tantalum alone.

Experimental Procedure for Determination of Tantalum in Titanium Alloys. 0.1 g of titanium alloy is dissolved on heating in 20 ml sulfuric acid 1 : 1. After the alloy has been dissolved the solution is oxidized with 25 % ammonium persulfate solution until the violet color of the solution changes to orange. The solution is heated until the solution is colorless. If the solution is turbid as the result of hydrolysis of tantalic acid, it is essential to add ammonium persulfate until the yellow color appears, and then the solution heated again until white fumes of sulfuric acid appear and the precipitate of tantalic acid has dissolved. 10 ml of 20 % tartaric acid is added to the cooled, colorless solution. This solution is transferred to a 100 ml standard flask and its volume made up to the mark with water. The solution is thoroughly mixed. 10 ml of this solution is pipetted into another standard flask with a capacity of 100 ml, and 20 ml of water and 5 ml of arsenazo solution added. A piece of Congo paper is placed in the solution and 10 % sodium carbonate solution added until the blue color of the paper changes to red (for neutralization of the sulfuric acid); 20 ml of hydrochloric acid 1 : 1 is then added and the solution mixed, it is finally transferred to a 50 mm photocolorimeter cell. Measurements are carried out using an orange filter (No. 6 FEK-N). The tantalum content is determined by means of a calibration curve. The calibration curve is constructed on the basis of a sulfuric-tartaric solution of tantalum on a background of 0.01 g titanium. The color of a 5 ml of arsenazo solution is determined in parallel under the same conditions. Readings for the blank test are subtracted from the readings obtained for the test solution.

The color of the tantalum compound is stable for a long time, but sulfuric-tartaric solutions of the titanium alloy which contain tantalum should not stand for more than 24 hours. It is best to take an aliquot part of the test solution on the same day that the titanium alloy is dissolved in acid.

SUMMARY

1. A photocolorimetric method has been developed for determination of tantalum by means of the reagent arsenazo in tartrate solutions. Arsenazo forms a soluble, violet colored compound with tantalum in strongly acid, preferably hydrochloric acid solutions. The tantalum-arsenazo complex is formed in tartrate and citrate solutions, and is stable on heating to 100°.

2. It has been found that the complex formed between titanium and arsenazo is completely destroyed in strongly acid hydrochloric acid solutions, and does not interfere with the photocolorimetric determination of tantalum with arsenazo from the tantalum tartrate complex.

3. A simple and rapid method has been developed for the photocolorimetric determination of 1-15 % of tantalum by means of arsenazo in titanium alloys, without preliminary separation of titanium.

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ORGANIC COPRECIPITANTS

COMMUNICATION 8. COPRECIPITATION OF URANIUM DURING ITS DETERMINATION IN SEA WATER*

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The present article contains a description of the coprecipitation of uranium from sea water, with its simultaneous separation from salts dissolved in the sea water. A number of elements, which are present in sea water in very small concentrations, are coprecipitated with uranium.

The uranium content of sea water is so small that its direct determination in the water itself, or in the dry residue left after evaporation, has not been achieved. Various techniques can be used for preliminary concentration. Small amounts of uranium can be separated by precipitating it with ferric or aluminum hydroxide [1, 2], or with iron and aluminum phosphates [3]. A method was described recently [4] for concentrating uranium by means of dibutylorthophosphoric acid. Coprecipitation with organic coprecipitants is particularly suitable.

In the presence of excess thiocyanates, uranium forms a weakly dissociating thiocyanate anion $[UO_2(SCN)_3^-]$ [5] in acid media, as a consequence of which, in accordance with the general rules [6, 7, 8], uranium can be coprecipitated with the precipitates of the sparingly soluble thiocyanates of heavy organic cations, such as the thiocyanates of the so called basic dyes (Methyl Violet, Crystal Violet, Methylene Blue, Rhodamine, Safranin, and many others). Coprecipitation of uranium as the thiocyanate anion proceeds quantitatively even from very dilute solutions of uranium (Table 1).

TABLE 1

Coprecipitation of Uranium with Methyl Violet Thiocyanate from Solutions of Pure Uranium Salts
(Volumes of the original solutions 100-1000 ml; 2.5 ml of a 40% solution of NH_4SCN and 5 ml of a 2 % solution of Methyl Violet were added to each 100 ml of solution)

Experiment number	Dilution of U	U coprecipitated, in %
1	$1:5 \cdot 10^8$	99
2-4	$1:1 \cdot 10^9$	100; 100; 101
5	$1:2 \cdot 10^9$	100
6	$1:5 \cdot 10^9$	100
7-9	$1:1 \cdot 10^{10}$	100; 101; 101

The results given in Table 1 were obtained during coprecipitation from pure solutions of uranium by means of the method described below. Determinations were carried out radiometrically using the radioactive isotope U^{233}, which is an α-emitter with a half-life period of 1.6×10^5 years. When an ordinary α-counter (standard issue) with a disc of diameter 40 mm was used, 1 γ of U^{233} gave 2200 impulses/minutes, for the geometry used. This permitted the determination of down to 0.04 γ U, so that when working with volumes of 1 liter it was possible to investigate the coprecipitation of uranium from its solutions at dilutions of $1:1 \times 10^{10}$. The organic precipitates were ashed in a muffle at 500-600° in No. 2 porcelain crucibles; the latter were of the short type with a height of about 20 mm and un upper diameter of about 25 mm.

Purification of Reagents

Precipitates of Methyl Violet thiocyanate coprecipitate uranium so effectively during their formation that this technique can be used for purifying the reagents to be used from traces of uranium.

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* Communication 7. Coprecipitation of Bi, G. Anal. Chem. 11, 686 (1956).

Completeness of purification was checked as follows: two solutions A and B were prepared.

A. 500 ml water
4.5 ml of approximately 11.5 N HCl
(d = 1.18)
120 ml of a 5 % solution of Methyl
Violet

B. 500 ml water
4.5 ml of approximately 11.5 N HCl
(d = 1.18)
25 ml of a 40 % solution of
NH_4SCN

To each solution was added U^{233} in amounts corresponding to 750 calculated impulses per minute, after which 20 ml of solution A was poured into another vessel, and to the residue was added slowly, with stirring, 50 ml of solution B. The 20 ml of solution A poured off was, in the same way, added to the residue of solution B. In both cases, dark precipitates (No. 1 and No. 2) were formed, these were filtered carefully twice, after which the corresponding filtrates were mixed. As a result of this mixing a large precipitate (No. 3) was formed, this was also filtered off, and then ashed; the activity of the residue from precipitate No. 3 was equal to 14 impulses, which corresponds to less than 1 % of the activity introduced.

The purification technique employed therefore guarantees complete removal of uranium from the reagents used. Experiments Nos. 7-9 in Table 1 were carried out with reagents which had been purified in this way. For these experiments two solutions were prepared corresponding in composition to solutions A and B (500 ml of water in each), 20 ml of solution A was added to B, while 50 ml of solution B was added to the residue of solution A. To the filtrates obtained by careful filtration of the precipitates formed, was added the requisite amount of U^{233}, and coprecipitation realized by mixing these solutions.

TABLE 2

Coprecipitation of Uranium with Methyl Violet Thiocyanate from Salt Solutions and Sea Water (Volumes of original solutions 400 ml, except for experiments Nos. 11, 12, 16, 17, 26, and 27, where the volume was 1000 ml; in the experiments designated by "+ ", after the pH had been adjusted to 1 the mixture was heated on a water bath for one hour)

No. of experiment, in order	Test material	pH	Uranium added, in γ	Dilution of the uranium	Uranium coprecipitated	
					Radiometric determination, as a % of that introduced	Fluorometric determination, in γ*
1	Salt solution	0.3	0.4	$1 : 1 \cdot 10^9$	93	–
2	Salt solution	0.7	0.4	$1 : 1 \cdot 10^9$	94	–
3, 4	Salt solution	1	0.4	$1 : 1 \cdot 10^9$	98; 100	–
5	Salt solution	1.3	0.4	$1 : 1 \cdot 10^9$	98	–
6	Salt solution	2	0.4	$1 : 1 \cdot 10^9$	100	–
7	Salt solution	3	0.4	$1 : 1 \cdot 10^9$	98	–
8	Salt solution	4	0.4	$1 : 1 \cdot 10^9$	95	–
9	Salt solution	5.5	0.4	$1 : 1 \cdot 10^9$	70	–
10	Salt solution	1	0.04	$1 : 1 \cdot 10^{10}$	98	–
11-12	Salt solution	1	0.1	$1 : 1 \cdot 10^{10}$	95; 98	–
13-15	Salt solution	1	0.4	$1 : 1 \cdot 10^9$	96+; 100+	–
16,17	Salt solution	1	1	$1 : 1 \cdot 10^9$	96; 100	–
18	Salt solution	1	0.4	$1 : 1 \cdot 10^9$	–	0.4
19	Salt solution	1	0.8	$1 : 5 \cdot 10^8$	–	0.8
20	Distilled water	1	–	–	–	0
21	Water from the Japanese sea	1	–	–	–	1
22	Water from the Japanese sea	1	0.4	$1 : 2.8 \cdot 10^8$	–	1.4
23-25	Water from the Japanese sea	1	0.4	$1 : 2.8 \cdot 10^8$	96; 96+, 100+	–
26	Water from the Pacific	1	–	–	–	1.7
27	Water from the Pacific	1	0.4	$1 : 5 \cdot 10^8$	–	2.2

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* Uranium was determined by the fluorescence method by L. L. Leonova (GEOKhI Acad. Sci. USSR).

Separation of Uranium from Sea Water

The pH of sea water is usually about 7-8. At this pH, uranyl ions should be present in the hydrolyzed form. Uranium may also be adsorbed or bound by the tissues of plankton organisms. The latter do not introduce difficulties during coprecipitation, since any uranium combined in this way will be filtered together with the plankton organisms. It is best to get the hydrolyzed uranium already present in the form of colloidal solutions into the form of true solutions, since coprecipitation presumes that the uranium is in the form of complex thiocyanate anions, not as colloidal particles. The hydrolysis products of uranyl salts do not lose their capacity to dissolve readily on acidification, when they are allowed to stand. Consequently, simple acidification of sea water can be regarded as quite sufficient for transforming the uranium into an ionic state.

In experiments which we carried out on the coprecipitation of uranium from slat solutions approximating in composition to sea water, and containing 28 g of NaCl, 1.7 g $MgSO_4 \cdot 7H_2O$, and 5.2 g of KCl per liter, the effect of pH on coprecipitation of uranium was studied.

In order to get a closer approximation to the natural state of uranium in sea water, the solutions were heated on a boiling water bath for 4-16 hours after addition of the uranium; after this, the solutions were acidified with hydrochloric acid until the pH was 1, this solution in turn was then heated on a boiling water bath for one hour or left for 2-3 hours at room temperature. Uranium was then coprecipitated from the solutions prepared in this way. Table 2 contains results obtained during determination of uranium both in sea water (Japanese Sea and Pacific Ocean), and in salt solutions approximating in their composition to sea water. Uranium was determined radiometrically or by the fluorescence method based on NaF beads [2] using an FM-42 fluorimeter. During determination of uranium by the fluorescence method, a correction was applied for extinction of the fluorescence.*

The method recommended for concentrating uranium from sea water was used in the work of the Soviet Antarctic Expedition[1956-1957] (V. M. Kutiurin, Diesel Electric Vessel "Ob").

Selective Action of the Organic Precipitant Used

All those elements which can form complex thiocyanate anions or insoluble thiocyanates, i.e., Hg, Ag, Bi, Zn, Cd, Mo, Fe^{III}, and some other elements, are partially or completely separated with the uranium. Since the content of all these elements in sea water is very insignificant, their coprecipitation during subsequent determination of uranium does not introduce any difficulties.

Trapping of a number of other elements can be essentially diminished by carrying out coprecipitation in the presence of Complexone III. Contamination by iron can be decreased by using purer Methyl Violet, or, by converting iron into the divalent state by addition of ascorbic acid or any other suitable reducing agent.

The Method Used for Concentrating Uranium from Sea Water

To a 1000 ml sample of sea water is added 9 ml of concentrated hydrochloric acid, and the solution left to stand for 2-3 hours. 25 ml of a 40% solution of ammonium thiocyanate is then added, and the whole thoroughly mixed; next, 50 ml of a 2 % aqueous solution of Methyl Violet is added slowly, dropwise with stirring, in the course of 20 minutes. After one hour the black precipitate is filtered off through a paper filter, moistened beforehand with wash solution. The precipitate is washed twice with the same wash solution, it is then transferred to a porcelain crucible and dried, next, it is moistened with a few drops of diluted H_2SO_4 (1 : 1) and slowly ashed at 500-600°, taking all the necessary precautions to prevent any mechanical loss during ashing. Uranium is then determined in the residue obtained after ashing.

This technique permits concentration of uranium from solutions at dilutions of the former of $1 : 1 \times 10^{10}$ (0.1 γ/liter).

The wash solution is prepared as follows. To 400 ml of distilled water is added about 2-3 ml of concentrated hydrochloric acid, about 1 g of NH_4SCN, and about 2 ml of 2 % Methyl Violet solution.

The authors wish to thank L. M. Khitrov and V. P. Tamont'ev for samples of sea water, and L. L. Leonova for carrying out the fluorometric determination of uranium.

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* The necessity of introducing a correction was the result of the presence of iron in the Methyl Violet used, this was partially precipitated with the precipitate of Methyl Violet Thiocyanate, and, on using 4 g of NaF decreased the intensity of the fluoresence by an average of 7-10%.

SUMMARY

On addition of ammonium thiocyanate and Methyl Violet to acidified sea water, the precipitate of Methyl Violet thiocyanate which is formed, quantitatively coprecipitates any uranium present at dilutions of this metal down to $1 : 1 \times 10^{10}$. The precipitate formed is filtered off, and ashed. The residue then contains the coprecipitated uranium which has been separated from the sea water.

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POLAROGRAPHIC DETERMINATION OF URANIUM IN THE PRESENCE OF VANADIUM AND IRON

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Uranium is normally determined polarographically on the basis of its first wave with a half-wave potential of –0.2 volt (with respect to the saturated calomel electrode), the height of this wave being proportional to uranium concentration in neutral and weakly acid solutions. Trivalent iron is reduced to the divalent state in acid solutions at the zero value of the dropping mercury electrode, thereby covering the polarographic wave of uranium. Divalent iron gives a polarographic wave for reduction to the elemental state at dropping electrode potentials which are considerably more negative than –1 volt (saturated calomel electrode), and has no effect on the uranium wave [1-4]. Consequently, interference by iron can be eliminated by simply reducing the iron beforehand to the divalent state.

Quinquevalent vanadium whose wave in acid solutions already starts to develop at low positive dropping electrode potentials, also interferes with measurements of the uranium wave height. Quadrivalent uranium only gives a polarographic wave at potentials approximating to –1 volt (saturated calomel electrode). Nevertheless, in the presence of quadrivalent uranium, the limiting reduction current of uranium is not proportional to its concentration, so that it is not possible to carry out a direct determination of uranium by measuring the wave height.

We have shown [5] that the increase in the limiting current for the reduction of uranium is determined by the chemical reaction of the oxidation of quinquevalent uranium by quadrivalent vanadium which occurs on the electrode surface.

We have developed two variants of a technique for carrying out polarographic determination of uranium in the presence of vanadium and iron; in the first of these, the effect of vanadium is eliminated by making the vanadium concentration in solution a constant; while the second variant provides for a preliminary electrolytic reduction of uranium and vanadium.

1. Polarographic Determination of Uranium in the Presence of Vanadium and Iron at a Constant Vanadium Concentration

In previous work, we have shown that there is no linear relationship between the limiting current of uranium and its concentration, in the presence of quadrivalent vanadium. All the same, the curves relating the limiting current of uranium and its concentration, at relatively high contents of quadrivalent vanadium, are readily reproducible, and can be used as calibration curves for determining the uranium content of solutions, on the basis of the value of the limiting current.

For polarographic determination of uranium in the presence of excess quadrivalent vanadium, it is essential to maintain the concentration of the latter in the test solution a constant. For this purpose, it is, therefore, necessary to determine the vanadium content beforehand, and to add to the solution that amount of vandium which will ensure the requisite value of its concentration in the final solution. The optimum vanadium concentration for the polarographic determination of uranium is 0.01 M.

In order to reduce vanadium and iron, the test solution is treated beforehand with a solution of sulfurous acid; excess SO_2 is removed by simple boiling.

Vanadium content is determined by titrating an aliquot of the test solution with potassium permanganate. The solution, after reduction, is therefore made up to constant volume. Too high a dilution leads to a decrease in sensitivity of the determination. The most convenient volume is 10 ml; lower volumes lead to difficulties in subsequent operations. Half of this solution is used for vanadium determination; to the remaining half is added the calculated amounts of standard solutions of quadrivalent vanadium and sulfuric acid, as well as a solution of potassium chloride, so that the total volume of the solution is 10 ml, and its concentration with respect to vanadium is 0.01 M, while it is 0.1 N with respect to KCl and H_2SO_4. This solution is used for the polarographic determination of uranium.

During the permanganometric determination of vanadium a small amount of ammonium persulfate should be added to the solution to oxidize iron [6] as well as some crystals of sodium phosphate.

TABLE 1

Taken, in mg			U found			V found		
U	V	Fe	mg	absol. error in mg	relat. error in %	mg	absol. error in mg	relative error in %
0.014	3.84	10.1	0.014	0	0	3.77	−0.07	1.8
			0.014	0	0	3.86	+0.02	0.5
0.057	4.16	136.8	0.059	+0.002	3.5	4.01	−0.15	3.6
			0.054	−0.003	5.3	4.20	+0.04	1.0
			0.055	−0.002	3.5			
0.087	7.84	7.2	0.087	0	0	7.55	−0.29	3.7
			0.087	0	0	7.69	−0.15	1.9
0.52	0.96	83.4	0.50	−0.02	3.8	1.02	+0.06	6.3
			0.51	−0.01	1.9	0.97	+0.01	1.0
			0.52	0	0			
0 98	9.60	77.8	0.96	−0.02	2.0	9.43	−0.17	1.8
			0.99	+0.01	1.0	9.57	−0.03	0.3
			0.94	−0.04	4.1	9.52	−0.08	0.8

Polarographic determination should be carried out in a thermostat which should be kept constant with an accuracy of at least 0.2°, since temperature changes affect the value of the limiting current strongly. Results for the determination of uranium and vanadium by this method are given in Table 1.

It should be noted that the given method for the polarographic determination of uranium differs from the usual polarographic methods in its increased sensitivity, which is determined by the presence of vanadium in solution leading to an increase in the limiting current for reduction of uranium. The sensitivity of uranium determination using as supporting electrolyte a solution containing 0.01 mole/liter $VOSO_4$, 0.1 mole/liter KCl, and 0.1 g.equivalent/liter H_2SO_4, is approximately ten times the sensitivity of uranium determinations in solutions with a different composition. The relative experimental error is not more than a few percent. The method can be recommended for the polarographic determination of uranium in solutions containing from 0.01 to 1 mg of uranium, at vanadium contents not exceeding 10 mg. These limits are set by the impossibility of measuring both too small, or too large values of the limiting current as the case may be.

2. Polarographic Determination of Uranium in the Presence of Vanadium and Iron after Preliminary Electrolysis of the Solution with a Mercury Cathode

The method described below is based on the preliminary reduction of the test solution on a mercury cathode, and on the further determination of the uranium content on the basis of the value of the limiting current of the anode-cathode wave U^{III}/U^{IV} at a half-wave potential of −0.97 volt (saturated calomel electrode). Vanadium is reduced to the divalent state, giving an anode wave at −0.5 volt. Even at very high vanadium concentrations (right up to a saturated solution of ammonium metavanadate), the polarographic current, after reduction on the mercury cathode, becomes equal to zero even at −0.6 volt, so that it becomes possible to measure the wave height for quadrivalent uranium in the presence of any amount of vanadium in solution.

Electrolysis on a mercury cathode as a method of separating a number of accompanying elements from uranium before polarographic determination of the latter has been used before [3], all the same, the polarographic wave of quadrivalent uranium was not used for analytical purposes because it lies at potentials approximating to the reduction potential of hydrogen ions. The successful application of the polarographic waves of both quadrivalent uranium, and of its mixtures with trivalent uranium, for the determination of uranium, becomes possible when the waves satisfy the following conditions: 1) the diffusion current must be proportional to uranium concentration; 2) the value of the diffusion current for a given uranium concentration is a constant for wide limits of the hydrogen ion concentration in solution; 3) the value of the diffusion current is independent of the ratio of the concentrations of quadri- and trivalent uranium, i.e. the system U^{IV}/U^{III} is reversible on the dropping mercury electrode, and the values of the diffusion coefficients of both ions are similar to each other.

The existence of a direct proportionality between the diffusion current and concentration of quadrivalent uranium in a medium of 0.1 N H_2SO_4 and 0.1 N KCl, is evident from Table 2.

TABLE 2

C_U mmoles/ /liter	i_d μA	$\frac{i_d}{C_U}\frac{\mu A}{mM/l}$	volt (sat. calomel electrode)
0.25	0.62	2.50	−0.968
0.50	1.24	2.48	−0.971
0.75	1.85	2.47	−0.972
1.00	2.52	2.52	−0.965
1.25	3.06	2.45	−0.970
1.50	3.80	2.53	−0.973

TABLE 3

$C_{H_2SO_4}$ N	i_d μA	$\frac{i_d}{C_U}\frac{\mu A}{mM/l}$	volt (sat. calomel electrode)
1.0	3.83	2.53	−0.971
0.5	3.80	2.53	−0.970
0.1	3.74	2.50	−0.974
0.01	3.49	2.32	−0.982
0.001	3.28	2.18	−0.983

Results of a study of the effect of the acidity of the solution on the polarographic wave of quadrivalent uranium (1.5 millimole/liter; 0.1 N KCl) are presented in Table 3.

It is clear from this table that the optimum sulfuric acid concentation is 0.1-0.5 N. In this acidity range, the uranium wave has a section which is convenient for measurement, while its height remains constant for a given uranium concentration.

TABLE 4

Duration of reduction, in minutes	i_d μA cathodic	i_d μA anodic	i_d μA total	$\varphi_{1/2}$ volts (sat. calomel electrode)	Rt/nF volt
10	3.75	0	3.75	−0.968	0.054
15	3.43	0.30	3.73	−0.972	0.057
20	3.18	0.56	3.74	−0.973	0.050
25	2.95	0.75	3.70	−0.968	0.056
30	2.56	1.16	3.72	−0.973	0.061

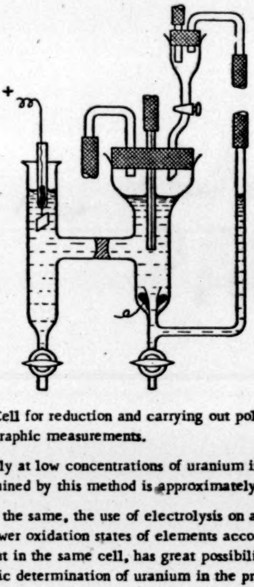
Analysis of the total wave for quadri- and trivalent uranium showed that the anode current of U^{III} and the cathode current of U^{IV} form a smooth and continuous curve. Table 4 contains results of measurements of the limiting current of such anode-cathode waves, obtained in solutions, containing quadri- and trivalent uranium in various proportions, the ratio of the two valence states was altered by changing the duration of reduction of uranyl sulfate (1.5 millimole/liter) on the mercury cathode. It is evident from the results given in this table that the value of the total limiting current remains a constant, independently of the ratio of the concentrations of U^{IV} and U^{III} in solution.

Thus, the results quoted show that the anode-cathode wave of the system U^{III}/U^{IV} can be used for the polarographic determination of uranium in the sulfuric acid concentration range 0.1 to 0.5 N.

Attempts at reducing ammonium vanadate on a mercury cathode, in sulfuric acid solutions, did not yield positive results, because of the formation of a white precipitate of mercury vanadate on the electrode surface during electrolysis, and this prevented the further course of the electrolysis. Consequently, vanadium should be reduced to the quadrivalent state before electrolysis.

TABLE 5

Taken in mg			U obtained in mg	Error	
U	V	Fe		Absol. in mg	Relative in %
0.40	40.0	147	0.40	0	0
			0.41	+0.01	2.5
			0.40	0	0
0.79	97 0	17.5	0.79	0	0
			0 81	+0.02	2.5
2.65	8.4	63.2	2.67	+0.02	0.8
			2.62	−0.03	1.1
			2.69	+0.04	1.5
5.29	101	78.5	5.14	−0.15	2.8
			5.45	+0.16	3.0



Cell for reduction and carrying out polarographic measurements.

The technique used for the polarographic determination of uranium in solutions containing vanadium and iron consists of the following. The test solution which has been acidified with a few drops of 1 N H_2SO_4 is heated, after which a few milliliters of a saturated solution of sulfur dioxide is added to it. The solution is boiled until all excess SO_2 has been removed.

The volume of the solution is made up to 10 ml; 3 ml of this solution is next transferred to a special cell, shown on the diagram, in order to carry out the reduction, and make polarographic measurements; 1.5 ml of 1 N H_2SO_4 is added to the contents of the cell. 5.5 ml of 0.3 N KCl is poured into the funnel fastened into the stopper of the cell. The anode space in which the platinum anode is placed is filled with 0.3 N H_2SO_4 solution. Electrolysis is carried out for 20 minutes at a potential of 16-24 volts; the solution is agitated by means of a hydrogen stream. When electrolysis is complete, the potassium chloride solution in the funnel is completely emptied (under hydrogen pressure) into the test solution, which is then cooled in the hydrogen stream to 25°. The solution in the anode compartment is connected through an electrolytic switch to a saturated calomel electrode, and polarograms are taken over the range −0.5 to −1.4 volt. The uranium content of the test solution is established from the value of the diffusion current of the wave for U^{IV}/U^{III} with a half-wave potential of approximately −1 volt, by using a calibration curve.

Results for the polarographic determination of uranium by this method are given in Table 5.

It should be pointed out that this method is less sensitive than other methods for the polarographic determination of uranium based on measuring the wave height of sexivalent uranium. The reason for this is related to the fact that the specific polarographic wave of quadrivalent uranium appears at dropping electrode potentials only 0.2-0.3 volt more positive than the reduction wave for hydrogen ions. This circumstance complicates measurement of the wave height for uranium, particularly at low concentrations of uranium in solution. The minimum, absolute amount of uranium which can be determined by this method is approximately 0.4 mg.

All the same, the use of electrolysis on a mercury cathode for the removal from solution, or for the reduction to lower oxidation states of elements accompanying uranium, with subsequent polarographic determination carried out in the same cell, has great possibilities, from the point of view of extending this technique to the polarographic determination of uranium in the presence of a number of other metals, in addition to vanadium and iron, which are reduced on the mercury cathode. Our preliminary experiments on the possibilities of determining uranium polarographically by this technique have shown that the presence of magnesium, aluminum, copper, titanium, and manganese, have no effect on the results of the polarographic determination of uranium, after preliminary electrolysis of the solution with a mercury cathode.

SUMMARY

1. A method has been developed for the polarographic determination of 0.1-1 mg of uranium in the presence

of vanadium and iron, which is based on the use of a solution containing a constant amount (0.01 mole/liter) of quadrivalent vanadium as a supporting electrolyte.

2. It has been shown that in sulfuric acid solutions, the anode-cathode wave of U^{III}/U^{IV} is suitable for polarographic determination of uranium, independently of the ratio of quadri- to trivalent uranium.

3. A technique has been developed for the polarographic determination of uranium in solution, in the presence of vanadium and iron, after preliminary electrolysis of the test solution with a mercury cathode. The method is suitable for the determination of absolute amounts of uranium which are greater than 0.4 mg.

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THE USE OF RADIOMETRIC METHODS FOR THE SIMULTANEOUS SEPARATE DETERMINATION OF THE CONTENT OF URANIUM, THORIUM, RADIUM, AND POTASSIUM IN ACID IGNEOUS ROCKS

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The studies were carried out on samples of Eldjurta granites from the Tyrny-Auz district. Both strongly weathered granites taken from the surface, as well as unchanged granites taken from deep bore holes and mines were used for these studies.

For the separate determination of the amounts of U, Th, Ra, and K in acid igneous rocks, the authors used a combination of α-, β-, γ-, and γ-discriminating measurements. As a result the following system of four equations were obtained:

$$\begin{aligned} A_\alpha &= \alpha_1 U + \alpha_2 Ra + \alpha_3 Th; \\ A_\beta &= \beta_1 U + \beta_2 Ra + \beta_3 Th + \beta_4 K; \\ A_{\gamma_1} &= \gamma_1 U + \gamma_2 Ra + \gamma_3 Th + \gamma_4 K; \\ A_{\gamma_2} &= Ra + \gamma_1' Th + \gamma_2' K. \end{aligned} \tag{1}$$

In these equations A_α, A_β, A_{γ_1} and A_{γ_2} are the activities of the test samples, expressed in equivalent percentages of the equilibrium uranium respectively for each type of measurement. α_1, α_2, α_3, β_1, β_2, β_3, β_4, γ_1, γ_2, γ_3, γ_4, γ_1' and γ_2' are the equivalents of equilibrium uranium for U, the Ra-group, Th, and K with respect to α-, β-, γ- and γ-discriminating measurements.

The position of the discriminator during γ-discriminating measurements was chosen so that the γ-radiation of the U group was not registered.

In order to solve the system of equations (1) by means of determinants, formulas were obtained for determining the content of each element.

$$U = \frac{D_U}{D_{\text{systems}}}; \; Th = \frac{D_{Th}}{D_{\text{systems}}}; \; Ra = \frac{D_{Ra}}{D_{\text{systems}}}; \; K = \frac{D_K}{D_{\text{systems}}}, \tag{2}$$

where

$$\begin{aligned} D_{\text{systems}} = {} & \alpha_1\beta_2\gamma_3\gamma_2' + \alpha_1\beta_3\gamma_4 + \alpha_1\beta_4\gamma_2\gamma_1' + \alpha_2\beta_1\gamma_4\gamma_1' + \alpha_3\beta_1\gamma_2\gamma_2' + \alpha_2\beta_3\gamma_1\gamma_2' + \\ & + \alpha_3\beta_4\gamma_1 - \alpha_1\beta_4\gamma_3 - \alpha_1\beta_2\gamma_4\gamma_1' - \alpha_1\beta_3\gamma_2\gamma_2' - \alpha_2\beta_1\gamma_3\gamma_2' - \alpha_3\beta_1\gamma_4 - \alpha_2\beta_4\gamma_1\gamma_1' - \alpha_3\beta_2\gamma_1\gamma_2'; \end{aligned}$$

$$\begin{aligned} D_U = {} & (\beta_2\gamma_3\gamma_2' + \beta_3\gamma_4 + \beta_4\gamma_2\gamma_1' - \beta_4\gamma_3 - \beta_2\gamma_4\gamma_1' - \beta_3\gamma_2\gamma_2') A_\alpha - \\ & - (\alpha_2\gamma_3\gamma_2' + \alpha_3\gamma_4 - \alpha_2\gamma_4\gamma_1' - \alpha_3\gamma_2\gamma_2') A_\beta + (\alpha_2\beta_3\gamma_2' + \alpha_3\beta_4 - \alpha_2\beta_4\gamma_1' - \\ & - \alpha_3\beta_2\gamma_2') A_{\gamma_1} - (\alpha_2\beta_3\gamma_4 + \alpha_3\beta_4\gamma_2 - \alpha_2\beta_4\gamma_3 - \alpha_3\beta_2\gamma_4) A_{\gamma_2}. \end{aligned}$$

$$D_{Ra} = (\beta_1\gamma_4\gamma_1' + \beta_3\gamma_1\gamma_2' - \beta_1\gamma_3\gamma_2' - \beta_4\gamma_1\gamma_1')\,A_\alpha + (\alpha_1\gamma_3\gamma_2' - \alpha_1\gamma_4\gamma_1' - \alpha_3\gamma_1\gamma_2')\,A_\beta -$$
$$- (\alpha_1\beta_3\gamma_2' - \alpha_1\beta_4\gamma_1' - \alpha_3\beta_1\gamma_2')\,A_{\gamma_1} + (\alpha_1\beta_3\gamma_4 + \alpha_3\beta_4\gamma_1 - \alpha_1\beta_4\gamma_3 - \alpha_3\beta_1\gamma_4)\,A_{\gamma_2},$$
$$D_{Th} = (\beta_1\gamma_2\gamma_2' + \beta_4\gamma_1 - \beta_1\gamma_4 - \beta_2\gamma_1\gamma_2')\,A_\alpha - (\alpha_1\gamma_2\gamma_2' - \alpha_1\gamma_4 - \alpha_2\gamma_1\gamma_2')\,A_\beta +$$
$$+ (\alpha_1\beta_2\gamma_2' - \alpha_1\beta_4 - \alpha_2\beta_1\gamma_2')\,A_{\gamma_1} - (\alpha_1\beta_2\gamma_4 + \alpha_2\beta_4\gamma_1 - \alpha_1\beta_4\gamma_2 - \alpha_2\beta_1\gamma_4)\,A_{\gamma_2};$$
$$D_k = (\beta_1\gamma_3 + \beta_2\gamma_1\gamma_1' - \beta_1\gamma_2\gamma_1' - \beta_3\gamma_1)\,A_\alpha + (\alpha_1\gamma_2\gamma_1' + \alpha_3\gamma_1 - \alpha_1\gamma_3 - \alpha_2\gamma_1\gamma_1')\,A_\beta -$$
$$- (\alpha_1\beta_2\gamma_1' + \alpha_3\beta_1 - \alpha_1\beta_3 - \alpha_2\beta_1\gamma_1')\,A_{\gamma_1} +$$
$$+ (\alpha_1\beta_2\gamma_3 + \alpha_2\beta_3\gamma_1 + \alpha_3\beta_1\gamma_1 - \alpha_3\beta_1\gamma_2 - \alpha_1\beta_3\gamma_2 - \alpha_2\beta_1\gamma_3)\,A_{\gamma_2}.$$

In formulas (2), U, Th, and K are obtained in percentages, while Ra is obtained as a percentage of equilibrium uranium.

The coefficients which enter into the original equations can be derived theoretically [2]. It is better, however, to obtain these coefficients experimentally, since, during theoretical calculations, it is not always possible to take into account the conditions under which the measurements are carried out and the characteristics of the apparatus used. The present authors determined the coefficients experimentally by using standard mixtures: of equilibrium uranium, pure uranoso-uranic oxide, (U_3O_8), thorium oxide (ThO_2), in which thorium was found in equilibrium with all the breakdown products, and potassium chloride and inactive materials.*

In order to obtain the exact values of the coefficients — as we found experimentally — it is necessary that the standard mixtures should satisfy the following requirements:

1. There should be equilibrium with fission products, and impurities in the form of other radioactive elements should be absent in the original radioactive material.

2. The emission coefficient for compounds of equilibrium U and Th should be low (not more than 10 %).

3. The composition of the enclosing substance during α-measurements should be the same (or similar in density and effective atomic number) as the composition during measurements based on β- and γ-rays. Any composition may be taken for the enclosing substance during determination of the coefficients as long as the composition remains a constant for all mixtures.

4. The distribution of the radioactive elements in the standard mixtures prepared should be uniform.

The values of the coefficients are practically independent of the content of radioactive elements in the standard mixtures. All the same, in order to ensure a more uniform distribtuion of the radioactive elements (which is particularly important during α- and β- measurements), and to increase the statistical accuracy at the time the observations are made, the authors recommend the use of mixtures with a high content of radioactive elements (up to a tenth of a percent of the original radioactive element).

The content of radioactive elements in mixtures during α-measurements should exclude errors arising from the apparatus counts.

The coefficients entering into equation (1) which we obtained relative to equilibrium uranium in mixtures with sodium carbonate, had the following values:

$\alpha_1 = 0.38$: $\alpha_2 = 0.62$: $\alpha_3 = 0.13$
$\beta_1 = 0.43$: $\beta_2 = 0.57$: $\beta_3 = 0.16$: $\beta_4 = 5.8\cdot10^{-4}$
$\gamma_1 = 0.016$: $\gamma_2 = 0.984$: $\gamma_3 = 0.32$: $\gamma_4 = 1.0\cdot10^{-6}$
$\gamma_1' = 1.1$: $\gamma_2' = 1.0\cdot10^{-4}$

Coefficient α_1 was obtained with a U_3O_8 mixture. Since the energy of α-radiation I_O is approximately equal to the energy of α-radiation U_I and U_{II}, half again of its value was added to the value obtained for the coefficient.

During α- and β-measurements the coefficients were obtained for saturated layers, while in the case of

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* The standard mixtures of equilibrium U and Th were checked by the absolute α-count method in infinitely thin layers.

γ-measurements the coefficients were obtained by measuring mixtures weighing 700 g.

During α- and β- measurements, the coefficients remained practically constant during the whole time of the work. The coefficients also remained constant during total γ-count, even for small changes (± 50-75 volt) in the working voltage applied to the FEU.

During discriminating γ-counts, however, the coefficients are considerably more dependant (up to 20 %) on the voltage applied to the FEU. The values of the coefficient for each type of measurement were subsequently checked not less than twice a month. The final equations for determining U, Th, Ra, and K, which were obtained by solving equations (2) and substituting the numerical values of the coefficients indicated above, are of the following form:

$$\begin{aligned} U &= 2.38\ A_\alpha + 0.29\ A_\beta - 1.9\ A_{\gamma_1} + 0.224\ A_{\gamma_2} \\ Th &= 0.046\ A_\alpha + 0.0096\ A_\beta - 1.35\ A_{\gamma_1} + 1.29\ A_{\gamma_2} \\ Ra &= 0.141\ A_\alpha - 0.178\ A_\beta + 1.45\ A_{\gamma_1} - 0.42\ A_{\gamma_2} \\ K &= -1980\ A_\alpha + 1680\ A_\beta + 360\ A_{\gamma_1} - 120\ A_{\gamma_2} \end{aligned} \qquad (3)$$

Results of measurements of samples were expressed in units of equilibrium uranium. Accordingly, particular attention was given to the choice of a uranium equilibrium standard. During a comparison of pure nonemitting equilibrium uranium ores which are normally used as standards with standard uranium standards it was established that the count rates for 1 % equilibrium uranium differed very strongly (up to 200 %) (See Table 1).

TABLE 1

Standard used (U content, in %)	Count rate, calculated for 1 % equilibrium U, on the basis of the results of:		
	α-measurements	β-measurements	γ-measurements
0.085	805,900	646,700	3,950,000
0.505	682,000	723,900	3,974,900
0.018		475,900	2,279,300
0.063	550,250	569,600	2,872,300
0.014 (standard)	770,000	550,000	2,883,400

These variations in the count rate, are, apparently, related to differences in the chemical composition of interfering material in the standards, and insufficiently reliable chemical analysis. In order to exclude errors arising from chemical analysis, special accurate uranium standards should be used as the uranium equilibrium standards.

Supplementary tests were carried out in order to evaluate the effect of differences in the chemical composition of the test materials (granites) and the standard uranium equilibrium mixture, on the results of the measurements. During α-measurements, differences in the count rate arising from differences in the chemical composition of the preparations amounted to 800 % (Table 2).

TABLE 2

Enclosing material	Count rate, in arbitrary units for different α-emitters		Enclosing material	Count rate, in arbitrary units for different α-emitters	
	U ($U_I + U_{II}$)	Th (equilibrium)		U ($U_I + U_{II}$)	Th (equilibrium)
Coal	242		Tellurium	1861	
Boron	314		Calcite	459	
Phosphorus	620		Sand	865	133
Iron	1777		Barytes	1000	143
Zirconium	1358		Galenite	1563	778
			Sodium carbonate	721	101

There are published references [1, 3] to the significant effect on results of α-measurements of the chemical composition of test materials when they are ground very fine, and when the radioactive elements are distributed uniformly in them (this was hardly completely accurately fulfilled in our case). The effect of the chemical composition on the results of β-measurements is significantly less, and can be illustrated by the results given in Table 3.

TABLE 3

Enclosing material	Sodium carbonate	Sand	Galenite	Lead sulfate ($PbSO_4$)
Count rate in impulses per minute for a U_3O_8 mixture on a type AS-2 counter............	620	625	880	850

From the tests carried out, it became evident that the composition of the uranium equilibrium standard should be very near to the composition of the test materials. The nearest in chemical composition to the test granites was quartz sand. The practically identical results obtained during β- and γ- measurements of mixtures with sand and sodium carbonate, permitted the use of sodium carbonate as an enclosing material for preparing uranium equilibrium standards for the measurements indicated. Sodium carbonate is practically inactive and it is far simpler to prepare than inactive quartz sand. For α-measurements the enclosing material used was quartz sand, since differences in count rate of up to 30% were observed for mixtures with quartz sand and with sodium carbonate respectively.

TABLE 4

Sample Number	Activity of the test samples in equivalent units of U for varying degrees of grinding		
	$0.25<d<0.5$	$0.1<d<0.25$	$d<0.1$
0-5	$12.3\cdot10^{-4}$	$11.9\cdot10^{-4}$	
0-6	$13.2\cdot10^{-4}$	$12.0\cdot10^{-4}$	
0-9	$13.2\cdot10^{-4}$	$12.8\cdot10^{-4}$	$11.0\cdot10^{-4}$
0-12	$18.0\cdot10^{-4}$	$16.3\cdot10^{-4}$	
0-13	$19.0\cdot10^{-4}$	$18.9\cdot10^{-4}$	$18.3\cdot10^{-4}$
0-72	$11.7\cdot10^{-4}$	$11.7\cdot10^{-4}$	$11.5\cdot10^{-4}$

Measurements of the test samples for determination of their U, Th, Ra, and K contents were carried out as follows: measurements of α-rays were made on a setup of the type Da-49 with an α-impulse cell of high sensitivity constructed by I. M. Nazarov. The increase in sensitivity was achieved by increasing the area of the electrodes at low (not more than 200 impulses/hour) values of the natural background; β-rays were measured on setup type B with an AS-2 counter placed in a lead housing; measurements of γ-rays were carried out on a scintillating γ-setup constructed by I. M. Nazarov and P. I. Solonkov. A NaI (Tl) crystallphosphor 40 mm in diameter and 50 mm high was used for the γ-measurements. Measurements of the test samples for their α-rays were carried out on a saturated layer on a plate with an area of 154 cm^2. The natural background hardly changed at all during the course of the day, consequently it was only determined at the beginning and the end of the work.

In order to check on the effect of degree of grinding of the standard on the results of α-measurements — the grain size of the standard being d 0.1 mm < d < 0.25 mm — and of the effect of the grain size of the test samples with a diameter d less than 0.5 mm, a number of test samples were measured for various grain sizes.

It follows from the results given in Table 4 that the particle size, within the limits indicated, does not have an essential effect on the results of α-measurements. Sample sizes of 50 g were used for β-measurements, the measurements being based on pure β-radiation (without γ). When this amount of test sample was placed on the plate, it was sometimes necessary to pack it. Studies of the effect of packing the test sample 1.5-2 times on the counting rate during β-measurements, showed that the count rate remains practically constant.

Samples weighing 150-500 g were used for γ-measurements, the amount depending on the amount of sample available. The natural background was determined after measuring each sample.

A check on the emission from samples of granites which had altered most (those taken from the surface) showed that the samples show practically no emission, consequently, no corrections for emission of test samples were introduced into the results for each type of measurement. The duration of observation for each type of measurement was chosen so that the relative error of the magnitude measured, determined by statistical variations, amounted to ± 5 %. On the basis of these considerations, the time during which samples were measured for α-radiation was

60 minutes, while the time taken to measure the natural background was 20 minutes. The time of observation for β-radiation was 30 minutes, and for total γ-radiation 5 minutes; the time for measuring background during total γ-emission was 2 minutes. The time of observation during γ-discriminating tests was 1.5 hours, and for the natural background in this case 1 hour.

TABLE 5

Uranium, Radium, Thorium, and Potassium Contents from the Results of Chemical, Radiochemical, and Radiometric Methods

Sample Number	$U \cdot 10^{-3}\%$		$Ra \cdot 10^{-10}\%$		$Th \cdot 10^{-3}\%$		K%		$\frac{Th}{U}$	$\frac{Ra \text{ in } U_{eq}}{U}$
	Chemically	Radiometrically	Radiochemically	Radiometrically	Radiochemically	Radiometrically	Chemically	Radiometrically		
05	3.7— 3.0	3.49	1.6	1.4	1.8	2.2	2.76	2 57	0.54	0.14
06		2.5	1.7	2.1	2.1	2.4	2.52	2 61	0.96	0.25
07	2.2; 2.2	1.92	1.6	2.1	1.9	2.12	3.67	3.87	0.87	0.22
08	3.7 2.0	3.4	2.1	2.17	2.0	2.06	2.84	2.94	0.7	0.22
09	2.3; 2.5	2.6	2.3	2.7	1.9	2.0	2.95	3.14	0.76	0.28
010	2.5; 1.9	2.3	1.9	1.57	2.4	2.37	2.36	2.42	1.09	0.25
011	3.7; 2.5	2.2	1.5	1.57	1.9	2.08	3.49	3.23	0.61	0.15
012	2.5; 1.8	2.2	2.0	1.83	2.2	2.5	3.28	3.25	1.02	0.28
013	2.5; 2.3	2.5	5.4	6.1	2.0	2.2	3.13	3.21	0.83	0.67
014	1.0; 1.0	1.4	2.3	2.03	1.9	1.8	1.62	1.57	1.9	0.69
Bore hole 35 meters 50		1.4	8.9	8.45	5.4	5.25	3.34	3.21	3.75	1.81
Bore hole 35 meters 100		4.0	3.6	3.77	2.4	2.05	3.56	3.64	0.51	0.28
Bore hole 35 meters 191		2.9	3.6	2.8	2.8	3.01	3.77	3.77	1.04	0.29
Bore hole 35 meters 240		1.86	3.4	3.9	2.6	2.87	3.81	3.49	1.54	0.63
Bore hole 35 meters 310		2.94	2.8	3.4	2.0	2.6	3.95	3.79	0.88	0.35
Bore hole 25 meters 348		3.14		2.2		2.88	2.91	2.77	0.92	0.21
061		0.89	2.1	5.3	1.6	1.2	3 19	3.2	1.35	1.8
062		1.61	2.6	1.5	1.6	2.8		4.5	1.7	0.28
063		1.31	1.75	3.3	1.5	0.47		4.3	0.35	0.76
Bore hole 34 meters 330		1.9	3.1	3.8	1.2	1.4		4.5	0.8	0.6
Bore hole 34 meters 367		1.5	4.3	4.5	1.4	3.2		3.3	2.1	0.9

The equilibrium uranium standard, relative to which the activity of test samples was measured, was measured for each type of radiation once in the course of a working day. The choice of the minimum observation time for test samples and for background in order to ensure a given accuracy, was carried out using the nomogram of Lovinger and Berman (diagram).

Results of determinations of the content of U, Th, Ra, and K by the method described, and by chemical and radiochemical analysis are given in Table 5.

The results of the radiometric analysis, are, as a rule, the mean of 2-3 measurements.

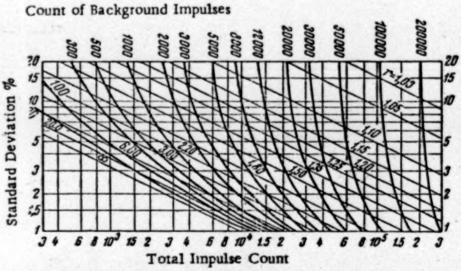
Chemical analysis for U by the luminescent bead method was carried out by N. Miroliubova and B. Karasev, while radiochemical determinations of Th and Ra — K were carried out by K. G. Kunasheva and A. P. Novitskaia. Potassium was analyzed chemically in the chemical laboratory of the Geotech Office of the Ministry of Non-Ferrous Metallurgy.

Evaluation of the accuracy of the results was carried out by means of the formula:

$$\varepsilon\% = \frac{1}{q_l\,\%}\sqrt{\Sigma\,(b_{ij})^2\,(\varepsilon_i)^2\,(A_l)^2} \tag{4}$$

where b_{ij} are the coefficients preceding A_{α}, A_{β}, A_{γ_1} and A_{γ_2} in equations (3) for each of the determined components;

ε_i is the relative statistical error of each measurement (in our case it was equal to ± 5%). A_l is the activity of the sample in equivalent units of U for each type of measurement; q_l is the content of the radioactive element being determined in %.



Nomogram for establishing the minimum count time to ensure measurements with a given error, for a known ratio of total count rate to background count rate.

In applying formula (4), the authors assumed that the accuracy of the determination of coefficient b_{ij} is one order higher — because it was determined repeatedly and accurately — than that of the accuracy of determination of the activity of the samples. The relative errors as calculated from formula (4) proved to be equal to:

$$\varepsilon_U = \pm 10\%;\ \varepsilon_{Th} = \pm 10\%;\ \varepsilon_{Ra} = \pm 20\%;\ \varepsilon_K = \pm 10\%.$$

The large error in determining the Ra content is readily explained, since variations in the coefficients during γ--discriminating measurements have a considerable influence on the accuracy of Ra determination.

SUMMARY

1. The article contains a description of a technique developed by the authors for the simultaneous separate determination of the U, Th, Ra, and K contents of acid igneous rocks.

Studies carried out on synthetic mixtures weighing 140 g and containing $6 \cdot 10^{-4}$ % U, $18 \cdot 10^{-4}$ % Th, $2 \cdot 10^{-10}$ % Ra and 9 % K, i.e. with a U content practically one order lower than in Eldjurta granites, showed that it is possible to get satisfactory results.

2. For the successful application of this technique for the separate determination of U, Th, Ra, and K contents in rocks, of basic importance is the correct choice of standards and the appreciation of all the factors which affect the results of measurements.

3. Separate determination of low contents of U, Th, Ra, and K can be carried out on any apparatus satisfying the following basic requirements: a) the apparatus must have high sensitivity (it should be sensitive to standards with a content of radioactive elements one order lower than that in the test samples); b) it should be stable in operation, thereby ensuring that the coefficients remain constant during the long time taken to make the measurements.

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A GRAVIMETRIC METHOD OF DETERMINING URANIUM USING CUPFERRON FOR ITS SEPARATION

S. V. Elinson and V. A. Olezniuk

Uranium which possesses a complex electronic configuration is a typical complexing agent. A large number of complex compounds of uranium are known with such organic reagents as α-nitroso-β-naphthol, isatin-β-oxine, urotropine, ammonium benzoate, tannin, pyridine, ethyelenediamine, quinaldinic acid, 8-hydroxyquinoline, cupferron etc. [1]. According to the studies of Duval [2] the precipitates formed with the reagents listed above change to U_3O_8 at a maximum calcining temperature of 946°. Of the published methods for determining uranium the method involving cupferron deserves special attention. Precipitation with cupferron can be carried out from comparatively acid solutions, in the presence of hydrofluoric acid and boric acid, and also in the presence of citric and tartaric acids. According to published results [3], cupferron precipitates iron, gallium, zirconium, niobium, tin, antimony, hafnium, titanium, vanadium, tantalum and quadrivalent uranium from sulfuric acid solutions; aluminum, chromium, manganese, zinc, nickel, beryllium, phosphorus, boron, sexivalent uranium. The alkaline-earth and alkali metals are not precipitated in acid media. Copper and thorium are precipitated in weakly acid media. In the analytical chemistry of uranium, separation by means of cupferron has been mainly used for removal of interfering elements during its titrimetric determination [4]. During gravimetric determination, sexivalent uranium is first precipitated with cupferron for its separation from iron, titanium, vanadium, and other elements, uranium is subsequently reduced to the quadrivalent state and is precipitated with cupferron for removing it from aluminum, chromium, beryllium, phosphorus, manganese, etc.

Holliday and Cunningham [5], after removing impurities from uranium, oxidized the cupferron by a repeated treatment with sulfuric and nitric acids, and then reduced the uranium in a Jones reducer, or by other methods, and precipitated the cupferronate of quadrivalent uranium. The cupferron method was subsequently used by other authors [6]. All the same, the gravimetric method, in the form suggested, cannot be used for analyzing ores and concentrates in mass production. Oxidation of excess cupferron with nitric and sulfuric acid is a long operation, demanding several treatments, and not always attaining the required ends. Using double precipitation with cupferron as a basis, we made it our aim to choose the analytical conditions such that the method would be rapid, simple, and suitable for the analysis of ores and concentrates under factory laboratory conditions.

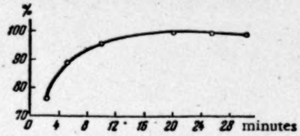
1. Choice of Reducing Agent. Amalgamated zinc, cadmium, or bismuth as used in the Jones reducer for reduction of uranium, proved to be unsuitable in the given instance, in view of the unavoidable precipitation of the cupferronate of the reduced uranium in the reducer. Syrokomskii and Klimenko [7] used divalent chromium for determining uranium. In order to check up on the possibility of using divalent chromium, various amounts of a standard uranyl solution (5-30 mg) were reduced with divalent chromium, the uranium was then precipitated with 4-5 ml of 6 % cupferron solution, and, after calcining the cupferronate to U_3O_8, the latter was weighed. Most of the results were high because 1-2 mg of chromium was trapped by the cupferronate precipiate. Sodium hydrosulfite ($NA_2S_4O_6$) was next tried as a reducing agent. To sulfuric acid solutions containing from 25-100 mg of uranium per 100 ml, and 4 % (by volume) of sulfuric acid, was added 1 g of dry hydrosulfite, the whole thoroughly mixed, and then allowed to stand for 15-20 minutes. Uranium was next precipitated with cupferron, small portions of a 6 % solution of the latter being added until the appearance of a rapidly disappearing fine white precipitate, in contrast to the flocculent, insoluble precipitate of the cupferronate (about 4-5 ml). The precipiate was filtered off, and washed with 120-150 ml of 4 % sulfuric acid containing 1.5 g cupferron in 1 liter of solution. After igniting and calcining, the U_3O_8 obtained was weighed.

TABLE 1

Determination of Uranium with Cupferron after Reduction with Hydrosulfite

Uranium taken, in mg	Uranium found, in mg	Error, in mg
25.45	25.5	+ 0.05
25.45	25.4	- 0.05
50.9	50.8	- 0.1
50.9	51.1	+ 0.2
101.3	102.1	+ 0.3
101.8	101.7	- 0.1
50.9	50.9	- 0

Results, which have been calculated in terms of uranium, are given in Table 1.



Relation between percentage reduction with hydrosulfite and time.

2. The Relation between Percentage Reduction and Time. Reduction of uranium with hydrosulfite is a time reaction. In order to determine the optimum conditions for carrying out the reduction, a series of tests were carried out with solutions containing equal amounts of uranium. After addition of hydrosulfite, precipitation with cupferron was carried out as described above.

It is clear from the diagram that satisfactory results are only obtained when, after addition of hydrosulfite to the solutions containing uranium (150-200 mg), they are kept for not less than 20 minutes. In practice, during the analysis of ores and concentrates, the samples to be reduced will contain considerably smaller amounts of uranium.

3. Effect of Impurities. The following experiments were carried out with a mixture of pure uranium salts and some of the impurities which occur most frequently in ores and concentrates, such as aluminum, iron, vanadium, etc. Precipitation of the impurities by means of cupferron was carried out from a solution containing 10 % by volume of of sulfuric acid, while in the filtrate, after dilution to a concentration of 4 % sulfuric acid, the uranium was reduced with hydrosulfite and then precipitated with cupferron.

TABLE 2

Determination of Uranium in Mixtures after Double Precipitation with Cupferron

Uranium taken, in mg	Added, in mg				Uranium found, in mg	Error, in mg
	Iron	Aluminum	Vanadium	Molybdenum		
38.2	2.1	–	–	–	38.2	0
38.2	21.2	–	–	–	37.9	- 0.3
19.1	–	2.4	–	–	19.2	+ 0.1
38.2	–	4.9	–	–	38.2	0
38.2	2.1	4.9	2.0	–	38.3	+ 0.1
38.2	2.1	4.9	2.0	–	38.2	0
19.1	2.1	4.9	2.0	–	19.0	- 0.1
38.2	2.1	4.9	2.0	4.0	38.7	+ 0.5
38.2	2.1	4.9	2.0	4.0	39.6	+ 1.4
19.1	2.1	4.9	2.0	4.9	20.0	+ 0.9

The results given in Table 2 show that when uranium, iron, aluminum, and vanadium are present simultaneously in solution, the other metals are separated from uranium quite well and the analytical results obtained are satisfactory. Molybdenum in solution leads to a sharp rise in the analytical results. Practically none of it is separated from uranium in strongly acid media (10 %), the molybdenum remaining is partially precipitated as the sulfide on addition of sodium hydrosulfite, and is then filtered off with uranium cupferronate and appears as MoO_3 on calcining the final precipitate. Some of the MoO_3 is evaporated, and, depending on the calcining conditions, the amount of volatilized oxide will vary. This is the reason for the varying results obtained when molybdenum is present in solution. Copper, lead, and other elements of the sulfide group will be precipitated as the sulfides similarly to molybdenum on addition of hydrosulfite. In those cases, therefore, when the ores and concentrates contain, in addition to other impurities, the elements just listed, the normal experimental procedure must be modified by the additional operation of precipitating the sulfides of copper, molybdenum, lead, and other elements by sodium thiosulfate. In order to check the efficiency of such a separation, 10 ml of a 10 % solution of sodium thiosulfate was added to 50-70 ml of a solution of a mixture of salts, the solution containing 10 % by volume of sulfuric acid. The solution was heated to the boiling point, and left on a hot plate for complete coagulation of the precipitate. After the precipitate had been removed, a 5 % permanganate solution was added until the final solution was pink (this was done to oxidize excess thiosulfate and some of the partially reduced elements); the subsequent procedure involving precipitation with cupferron was the same as before. The results of these determinations are given in Table 3. In the absence of other elements of the sulfide group, copper and molybdenum can be removed by one ammoniacal precipitation, as is normally done in analysis.

TABLE 3

Determination of Uranium after Removal of Sulfide Group Elements

Uranium taken, in mg	Added, in mg						Uranium found, in mg	Error, in mg
	Iron	Vanadium	Aluminum	Copper	Molybdenum	Lead		
50.9	21.2	5.0	9.8	10.0	8.0	10.0	51.3	+ 0.3
50.9	21.5	5.0	9.8	10.0	8.0	10.0	50.9	0
50.9	10.6	10.0	4.9	5.0	8.0	20.0	50.7	- 0.2
50.9	10.6	10.0	4.9	10.0	16.0	5.0	51.3	+ 0.4

4. Analytical Procedure. The method which we have developed for determining uranium in ores and concentrates consists of the following. 0.2-1 g of accurately weighed test material — the amount taken being dependant on the expected uranium content — is transferred to a heat resistant, conical flask, in which it is broken down with nitric acid, 10 ml of sulfuric acid (1 : 1) is then added, and the resultant solution heated until white fumes appear. The residue is diluted with water, the latter being added in such an amount that the sulfuric acid content of the final solution is 10 % by volume. The solution is heated until the salts are completely in solution, and, without preliminary separation of the insoluble residue (SiO_2), 0.1 N permanganate solution is added dropwise to the solution, which has been cooled beforehand, until there is a permanent rose color. Then, at a temperature not exceeding 18°* the cupferronates of the impurities in the uranium (Fe, V, Ti, etc.) are precipitated by addition

TABLE 4

Analysis of Preparation I

Sample weight in g	Uranium determ.		$a-x$	$(a-x)^2$
	In g	In %		
0.4998	0.2578	51.60	+0.03	$9\cdot10^{-4}$
0.5012	0.2588	51.63	0	0
5.5001	0.2591	51.81	−0.18	$324\cdot10^{-4}$
0.1276	0.0658	51.56	+0.07	$49\cdot10^{-4}$
0.2504	0.1294	51.67	−0.04	$16\cdot10^{-4}$
0.2529	0.1307	51.70	−0.07	$49\cdot10^{-4}$
0.5005	0.2578	51.50	+0.13	$169\cdot10^{-4}$
0.5006	0.2575	51.43	+0.20	$400\cdot10^{-4}$
0.2536	0.1313	51.77	−0.14	$169\cdot10^{-4}$
0.1276	0.0659	51.64	−0.01	$1\cdot10^{-4}$
		$a=51.63$		$\Sigma=1213\cdot10^{-4}$

$$\sigma=\sqrt{\frac{1213\cdot10^{-4}}{9}}=\pm0.116;\qquad \frac{\sigma\cdot100}{a}=\pm0.225$$

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* Our experiments showed that cooling the solution to 6-10° for precipitation of uranium cupferronate, as indicated in the literature, is optional.

of a 6 % aqueous solution of cupferron in small portions with stirring, until excess of the reagent is present, as indicated by the appearance of a rapidly disappearing, fine white precipitate, in contrast to the insoluble precipitate of the metal cupferronates. The washed precipitate (washing being carried out with a 10 % solution of sulfuric acid containing 1.5 cupferron per liter) is rejected, and the filtrate plus washings transferred to a 300 ml beaker, in which it is diluted with water to 200 ml (5 % with respect to sulfuric acid). To this solution is added 2 g of hydrosulfite and the mixture stirred with a rod, and then allowed to stand for 20 minutes. A second precipitation with cupferron is then carried out. When the precipitate has coagulated (after 15-20 minutes), it is sucked on an ashless filter on a small Buchner funnel. The precipitate is washed with a 4 % solution of sulfuric acid containing 1.5 g cupferron per liter, using 150 ml of this liquid for washing. The washed precipitate is transferred to a tared crucible in which it is carefully dried, ignited, and then calcined in the colder part of the muffle. It is finally calcined at 1000-1050°. If spectrographic analysis indicates that, in addition to the usual impurities, the samples also contain elements of the sulfide group (Cu, Pb, Mo, etc.), then, after decomposition of the samples, these metals are separated in the form of their sulfides by addition of 10 ml of a 10 % solution of sodium thiosulfate to 50-70 ml of the original solution, and heating. Having removed the sulfide precipitate, the solution is adjusted so that it is 10 % with respect to sulfuric acid, the cupferronates of the other impurities are then precipitated as described above.

TABLE 5

Analysis of Preparation II

Sample weight in g	Uranium determin.		$a - x$	$(a - x)^2$
	in g	in %		
0.4996	0.0343	6.86	−0.03	$9 \cdot 10^{-4}$
0.5011	0.0342	6.82	+0.01	$1 \cdot 10^{-4}$
0.5021	0.0339	6.76	+0.07	$49 \cdot 10^{-4}$
0.5000	0.0348	6.97	−0.14	$196 \cdot 10^{-4}$
0.5009	0.0341	6.80	+0.03	$9 \cdot 10^{-4}$
0.5038	0.0340	6.75	+0.08	$64 \cdot 10^{-4}$
		$\bar{a} = 6.83$		$\Sigma = 328 \cdot 10^{-4}$

$$\sigma = \sqrt{\frac{328 \cdot 10^{-4}}{5}} = \pm 0.081; \qquad \frac{\sigma \cdot 100}{a} = \pm 1.19\%$$

TABLE 6

Loss of Uranium in Filtrates and Wash Liquors

Sample weight, in g	Uranium content, in %	Uranium lost in the filtrate			
		Volume, in ml	Content in 1 ml, in g	Content in the whole volume, in mg	As a % of the aliquot taken
0.5007	56.46	300	Not detected	–	0
0.2527	56.57	350	$6 \cdot 10^{-7}$	0.21	0.08
0.5031	56.80	300	$1 \cdot 10^{-6}$	0.30	0.06
0.5006	51.43	250	$2 \cdot 10^{-7}$	0.07	0.01
0.5020	56.82	255	$1 \cdot 10^{-7}$	0.02	0.005
0.4996	51.59	415	Not detected	–	0
0.5012	51.63	400	$1 \cdot 10^{-6}$	0.4	0.08

5. Analytical Results. Using this technique a number of samples of ores and concentrates with uranium contents of more than 5 % have been analyzed (Tables 4 and 5). Values of 51.6 and 6.86 % U were found by the reducing and gravimetric peroxide methods. The mean square error (δ) are given in the Tables in order to evaluate the accuracy of the method.

In order to establish the loss of uranium during analysis of samples with high uranium contents, filtrates and wash liquors obtained after precipitation of the cupferronate of quadrivalent uranium, were analyzed by the luminescence method. The results given in Table 6 show that these losses should not essentially affect the experimental results obtained.

SUMMARY

1. A gravimetric method has been developed for determining uranium in ores and concentrates containing more than 5 % of uranium; it is based on removal of impurities by means of cupferron, followed by precipitation of quadrivalent uranium by the same reagent, after reduction by means of sodium hydrosulfite.

2. The method has been checked on pure uranium, on synthetic mixtures containing impurities which usually accompany uranium, and on ores and concentrates containing varying amounts of uranium. In all cases, satisfactory results were obtained.

3. The method can be used for precision analysis of ores and concentrates containing more than 5 % of uranium, under factory laboratory conditions. One determination takes 4-5 hours. Four samples can be analyzed simultaneously.

4. The accuracy (reproducibility) of the method is characterized by a mean square error of ± 0.3 % (relative) for samples containing 50 % uranium, and by mean squre error of 1.2 % (relative) for samples containing 5-10 % uranium.

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DETERMINATION OF URANIUM, THORIUM AND IONIUM IN SEA SILT

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Determination of radioactive elements in sea silt is of interest for solving a number of geochemical questions, in particular, questions relating to the determination of sedimentation rate, and evaluation of the age of the sea silt.

In recent years methods have been published for the determination of ionium and thorium in sea silt by radiography [1], and for the determination of thorium in minerals [2]. The first method has still not found wide application because of its complexity, while the second method cannot be used for determination of ionium in sea silt, since it was developed for minerals with a high uranium content, and consequently was designed for the analysis of milligram amounts of sample.

From a geochemical point of view it is desirable to have a method which would allow simultaneous determination of the three elements on one aliquot. The method described here permits this to be done in two days. In 1954, we published a method for the direct determination of ionium in sea silt [3]. Bearing in mind the fortunate circumstance that all three elements — ionium, thorium and UX$_1$ — are thorium isotopes, we modified our method in such a way that on the basis of the isotopes separated on the carrier, it is possible to determine uranium, thorium, and ionium. After supplementary purification, thorium is determined photometrically, using Kuznetsov's reagent thoron [4], while uranium is determined on the basis of the β-activity of UX$_1$, and ionium on the basis of its α-activity.

Essentially, the proposed technique reduces to decomposition of the sample by fusion with sodium peroxide and removal of impurities. The scheme suggested for separating the radioactive elements in the course of the analysis is outlined on Fig. 1.

Completeness of Isolation of Thorium Isotopes. Thorium isotopes, during all the stages, are found in the precipitate. This excludes losses as a result of adsorption. The suggested scheme of analysis was checked by using UX$_1$, Th(234), from the point of view of completeness of isolation, and, also with RaD — RaE and Po from the point of view of the radiochemical purity of the thorium isotopes. Since, in order to get complete purification of thorium from impurities, additional operations are included, completeness of separation of the thorium isotopes was checked again. For this purpose, during the analysis of 20 g of silt, to each 5 g was added an amount of UX$_1$ (indicator for Th) of known activity. After completion of the analysis and the combination of the four 5 g aliquots following thorium determination, the activity of the Fe$_2$O$_3$ on which the thorium isotopes had been deposited was determined. The results obtained (Table 1) show that when the analysis is carried out according to the scheme suggested, there is practically no loss.

Effect of Impurities on Determination of Thorium with Thoron. The first element to be determined in the course of the analysis is thorium. According to published results [1] the amount of this element in sea silt is about 10^{-4} %. V. I. Kuznetsov's reagent "thoron", which we selected for the photometric determination of thorium, has been studied fairly thoroughly [4, 5]. Titanium, hafnium, and zirconium give similar colors to thorium with this reagent. These three elements, however, are removed during the fluoride break down. Elements which have a characteristic color in hydrochloric acid (iron, copper, nickel, etc.) also interfere. But even such elements as aluminum and calcium, which do not have a characteristic color, all the same, during photometric determination of very small amounts of thorium (1-3 γ / ml), may distort the results by lowering the color intensity. Fluorides, sulfates, phosphates, etc. also interfere with the detection of thorium. Accordingly, an important stage in the analysis is the complete separation of all accompanying elements. In this connection therefore, before photometric determination, the thorium isotopes are separated without a carrier. Nevertheless, however carefully all the operations are carried out, impurities are always present. In order to study the effect of these impurities on the accuracy of determination of thorium, a known amount of thorium was added to an aliquot of silt which had already been analyzed by the proposed scheme, and the total amount of thorium then determined. The results obtained (Table 2) show that the amount of impurity that remains with the thorium does not essentially affect the final result. The error does not exceed ± 15%.

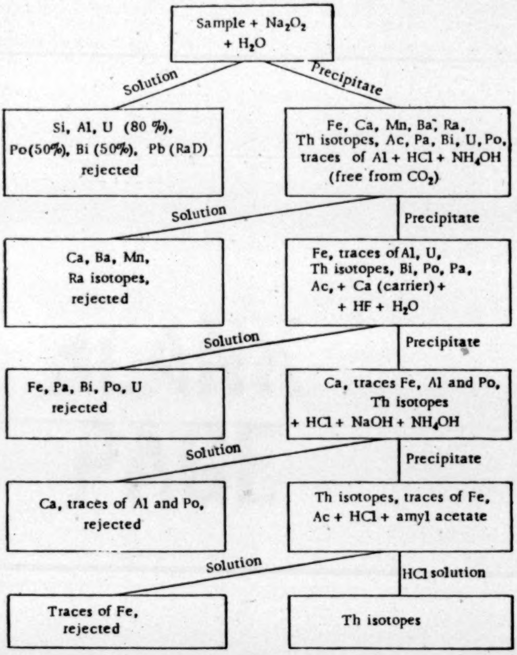
Sample + Na₂O₂ + H₂O
Solution
Precipitate
Si, Al, U (80 %), Po(50%), Bi (50%), Pb (RaD) rejected
Fe, Ca, Mn, Ba, Ra, Th isotopes, Ac, Pa, Bi, U, Po, traces of Al + HCl + NH₄OH (free from CO₂)
Solution
Precipitate
Ca, Ba, Mn, Ra isotopes, rejected
Fe, traces of Al, U, Th isotopes, Bi, Po, Pa, Ac, + Ca (carrier) + + HF + H₂O
Solution
Precipitate
Fe, Pa, Bi, Po, U rejected
Ca, traces Fe, Al and Po, Th isotopes + HCl + NaOH + NH₄OH
Solution
Precipitate
Ca, traces of Al and Po, rejected
Th isotopes, traces of Fe, Ac + HCl + amyl acetate
Solution
HCl solution
Traces of Fe, rejected
Th isotopes

Fig. 1. Analytical scheme

Determination of Uranium and Check on Completeness of Removal of RaD − RaE. Uranium was determined on the basis of UX_1 which is almost invariably found in equilibrium with its parent element. Since the uranium content of sea silt is about 10^{-4} %, the original aliquot taken should not be less than 15-20 g in order to get measureable β-activity. Under such conditions, measurements of both the preparation itself and of the background should be carried out for not less than 2-3 hours in order to get the required accuracy (10-15%). A sample weight of 20 g is decomposed in 4 lots of 5 g, each quarter being treated separately, right up to the point where thorium is determined. After the thorium has been determined all four solutions are combined, and the amount of thorium isotopes, precipitated on the iron, measured by means of a β-counter. The uranium content is calculated by means of a standard curve which is constructed on the basis of samples containing known amounts of uranium.

TABLE 1

Completeness of Isolation of Thorium Isotopes

Amount of Th introduced, in terms of impulses/ minute	Amount of Th found, in impulses/ minute	Th isolated, in %
1600	1580	99
1552	1474	95
1480	1471	99
1344	1323	98
1453	1470	101
1226	1185	96
1453	1492	103
1300	1280	98
1300	1200	92
1300	1320	101
1300	1270	98

TABLE 2

Determination of Thorium in Synthetic Samples (3.0 γ of Th was found in 2 g of silt)

Amount of Th (in γ) added to 2 g of silt	Amount of Th found, in γ
3.0	6.0
3.0	6.5
3.0	6.0
3.0	7.0
5.0	7.5
5.0	8.0
5.0	8.0
5.0	7.5

TABLE 3

Purity of Separation of RaD – RaE

RaD – RaE introduced, in terms of impulses/ / minute	RaD–RaE found, in terms of impulses/ minute	RaD – RaE as impurity in Th isotopes, expressed as a percentage of the latter	Observation	RaD – RaE introduced, in terms of impulses/ / minute	RaD – RaE found, in terms of impulses/ minute	RaD – RaE as impurity in Th isotopes, expressed as a percentage of the latter	Observation
10823	894	8.2	One fluoride treatment	10944	214	1.9	Two fluoride treatments
10950	860	8.0		10576	190	1.8	
10576	733	7.0		10576	132	1.2	
8844	420	4.8		8844	32	0.4	
10823	410	3.8		8844	74	0.8	
				8844	70	0.8	

During determination of uranium by this method, the ones which will obviously present the greatest trouble will be the β-active radiators ThB (Pb), RaD (Pb) and RaE (Bi), since the other natural β-emitters: RaB (T = = 26.8 minutes); RaC (T = 19.7 minutes); MsTh II (T = 6.13 hours); ThC (T = 60.5minutes); AcB (T = 36.0 minutes); AcC (T = 2.16 minutes), of all three radioactive series, are short lived and will decompose practically completely by the end of the analysis. Consequently, the fundamental problem is the complete removal of lead and bismuth isotopes. Lead is mainly removed in the first stage during fusion with sodium peroxide, and is removed again during precipitation of the hydrated oxides of iron and the Th isotopes by alkali. Bismuth is removed during the fluoride breakdown. This fact was established using silts which had been specially charged with a high RaD – RaE activity. An amount of RaD – RaE of known activity was added to a sample of silt before fusion. The final Fe_2O_3 precipitate was measured for its activity on a torsion β-counter. The results obtained (Table 3) show that when one fluoride treatment is given, not more than 7-8 % RaD - RaE remains with the thorium isotopes on the iron, while when a double fluoride treatment is given, the amount of adsorbed RaD - RaE does not exceed 2 %.

Determination of Ionium and Checking Completeness of Polonium Isolation. After the uranium has been measured, the ferric oxide is spread out on a disc as a fine even layer from acetone, and the ionium measured on a DA type α-counter. When the thorium content is high, a correction for its α-activity which is determined by Th + RaTh must be applied. Since ionium is determined on the basis of an α-count, the greatest danger is presented by uranium, polonium, radium, etc. During the analysis, uranium and polonium are removed together with lead in the first stage of the analysis, and are subsequently removed during the fluoride breakdown, polonium is also removed further during reprecipitation of the hydrated oxides with alkali. Radium is removed during the double treatment with ammonia. A check on the completeness of removal of polonium was carried out specially on samples which had been loaded with polonium before fusion (Table 4).

TABLE 4

Completeness of Polonium Removal

Po introduced, in terms of impulses/ minute	Po found in terms of impulses/ minute	% contamination of Th isotopes by ionium	Po introduced, in terms of impulses/ minute	Po found in terms of impulses/ / minute	% contamination of Th isotopes by ionium
7650	120	1.6	7650	175	2.3
7650	430	5.6	3456	4	0.2
7650	262	3.4	3456	10	0.1
7650	283	3.7	3450	30	1.0
7650	381	4.8	3456	6	0.2
7650	425	5.6			

Thus, by using the radioactive indicators UX_1, RaD, RaE, and Po, it was shown that isolation of thorium isotopes by the suggested analytical scheme proceeds quantitatively, and in radiochemically pure form. The errors which arise during determination of uranium and ionium, as a result of breakthrough of RaD - RaE and polonium, are, on the average + 1.1 % and + 2.4 % respectively.

TABLE 5

Uranium, Thorium, and Ionium Contents of Several Samples of Sea Silt

Station number.	Th content, in γ/g	U content, in γ/g	Io content, in uranium units	Error in Th determination, in %
3128	0, 6 0, 6 0, 65	3.6	1.0	± 8
3128	0, 6 0, 7 0, 6	3.0	1.1	± 8
3148	0, 9 1, 1 1, 2 1, 0	2.7	14.0	± 14
3138	1, 1 1, 2 0, 9 1, 0	2.6	3.0	± 14
619 (depth 300 cm)	4, 4 4, 8 – –	2.4	23.0	± 9
2218 (140 cm)	2, 7 3, 0 2, 4	1.20	2.0	± 11

Determination of Uranium, Thorium, and Ionium in Sea Silt. The method developed for the determination of uranium, thorium, and ionium has been used for studying the radioactivity of ocean silt. The results obtained (Table 5), show good agreement between the results and the accuracy of the determination is high, particularly for thorium. Each figure quoted for uranium and ionium was obtained on the basis of four parallel aliquots of 5 g each. Completeness of isolation was controlled on the basis of the agreement between the parallel determinations of thorium.

Thus, the results obtained show that the error in determining uranium, thorium, and ionium for thorium contents in the range 5×10^{-5} % to 10^{-4} % does not exceed 15 %. The error in determining uranium and ionium also varies by about 15 %.

Limits of Applicability of the Method and Additional Checking of the Radiochemical Purity of the Thorium Isotopes Isolated. We checked the method on a series of samples with known uranium contents ranging from 0.003 % (rocks) to 70 % (tar). The results obtained are given in Table 6 *. It is evident that when the

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* The thorium content of these samples was not determined.

analysis is carried out correctly, the uranium content as determined by both methods should coincide, since the half-life period of UX_1 is 24.3 days, which means that after 240 days there will be equilibrium between uranium and UX_1, and the UX_1 content will correspond to the uranium present. If the test samples are in a state of equilibrium, then the results of this column should coincide with the results in the two previous columns (in the Table).

TABLE 6

Determination of U and Io in Samples

Sample	U found, in %		Io found in uranium units, in %
	Chemically	Radiochemically, on the basis of UX_1	
Rocks	0.003	0.003	0.045
	–	0.004	0.006
	–	0.004	0.006
	0.02	0.018	0.018
	0.057	0.060	0.019
Ores	0.053	0.052	0.058
	0.390	0.380	0.450
	3.490	3.300	3.600
Tar	7.600	7.100	7.100
	70.000	67.000	69.000

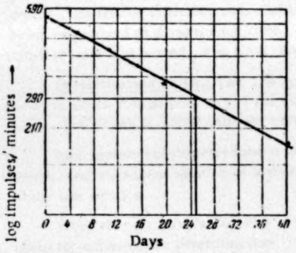

Fig. 2. Change in activity of UX_1 with time.

In our case, there was only one sample (No. 5) in which there was a breakdown in equilibrium with respect to ionium. It is obvious, therefore, that the given method can be applied for the determination of uranium and ionium, or the ratio Io/U for samples with a wide range of concentrations. For uranium contents of 10^{-3} %, the sample weight should be 4-5 g. During analysis of minerals a sample of 10-12 mg should be diluted with up to 0.5-1 g of rock (free from test elements) containing Si, Al, Fe, and Ca. The accuracy of an analysis is 10 % on the average.

During work with ores and minerals, removal of radioactive α- and β-contamination become particularly important since their content is so high. If insufficient care is taken during the analysis, the final result may be far too high. In this connection, therefore, during analysis of minerals, one further check was carried out on the radiochemical purity of the isolated ionium and uranium UX_1. Since the criterion for the radiochemical purity of the thorium isotopes with respect to α-activity is the constancy of the α-activity of the isolated ionium with time, while the criterion for the radiochemical purity of the isolated UX_1 is the regular fall in α-activity with time with a period TUX_1 = 24.3 days, the preparations which we isolated were measured for both their α- and β-activity with time. The results obtained are given in Table 7 and on Fig. 2. The constancy of the α-activity over a period of 5 months and the regular fall in UX_1, show that the thorium isotopes are actually isolated in a radiochemically pure form.

TABLE 7

Constancy of the Activity of Io with Time

Time, in days	Sample I, impulses/ / minute	Sample II, impulses/ / minute	Sample III, impulses/ / minute
7	820	–	288
10	800	218	302
20	830	215	–
35	810	222	290
60	820	–	287
95	788	236	–
118	809	220	300
150	813	210	–

EXPERIMENTAL

Isolation of Th Isotopes. A 5 g sample of dried silt is heated and fused with Na_2O_2 (6-10 times the amount of sample) in a nickel crucible. After the crucible has been cooled, the melt is leached with hot water (in a beaker of about 1.5 liters capacity). After standing for 10-15 minutes, the precipitate is filtered through a folded filter, and washed with hot water and dissolved on the funnel. The solution is collected in a platinum basin in a small volume of HCl (1 : 1). To this solution is added 50-70 mg $CaCl_2$ (as a solution) and the whole evaporated to dryness, the dry residue is treated with hydrofluoric acid (20-30 ml) and the whole again evaporated to dryness. The fluorides are moistened with 0.5 -1.0 ml of concentrated HCl and treated with hot water, the whole is then transferred to a 100 ml beaker, the precipitate is allowed to settle and is filtered through a folded "white ribbon grade" filter. The precipitate is washed, and then washed off the filter paper into a platinum basin in which it is evaporated, and then treated with $HClO_4$ until the thick white fumes cease to be evolved. The residue is again treated with HF and then evaporated and finally dissolved in hot water; it is next filtered, washed, and washed off the filter paper into the platinum basin. In this it is evaporated again, and the fluorides broken down by a double treatment with $HClO_4$. The residue is treated with concentrated HCl (5 ml) and heated until it dissolves, when it is transferred to a 100 ml beaker in which it is diluted with water to 50 ml. 5 g of NH_4Cl is added followed by ammonia (free from CO_2)[*] to effect precipitation.

The precipitate is filtered off, washed, dissolved in HCl (1 : 1), twice reprecipitated with NaOH (25 %), and then precipitated once again with NH_4OH with addition of NH_4Cl (5 g). The final precipitate is dissolved in a small volume of HCl (1 : 1) in a breaker and the solution evaporated to dryness, the dry residue is dissolved in HCl (2 ml of H_2O for 10 ml of concentrated HCl) and the solution transferred to a separating funnel, in which the iron is removed by means of amyl acetate saturated beforehand with HCl of the same concentration. The hydrochloric acid solution, which now only contains Th isotopes and traces of accompanying elements, is evaporated to dryness, the residue is treated twice with concentrated HNO_3, and then with 5 ml of concentrated HCl, the solution being evaporated to dryness each time. If the iron is not completely removed the first time, the removal with amyl acetate is repeated. The final dry residue is dissolved in 1 % HCl.

Determination of Th. The 1 % hydrochloric acid solution of the Th isotopes is transferred to a colorimeter tube, in which it is diluted to 5-7 ml with water; thoron (a 0.1 % solution) is added until the rose color is obtained, when more thoron is added until the color of the solution changes from rose to orange.

Into another colorimeter tube is added a 1 % hydrochloric acid solution, followed by the same amount of thoron, and a standard solution of a thorium salt until the color of the standard solution is comparable to the color of the test solution.

When the test sample contains more than 20 γ Th, the test solution is diluted in a standard flask and an aliquot taken for colorimetric determination.

Determination of U[**]. The contents of the colorimeter tube, after determination of Th, are transferred to a beaker, 1 ml of concentrated HCl and 20 mg of $FeCl_3$ (in the form of a solution) are added, and the solution diluted to 50 ml. It is then heated, and precipitation effected with NH_4OH. The precipitate is filtered through a "white ribbon" ashless filter, it is then dried and ashed, it is next calcined and weighed, and its β-activity is measured on a torsion counter with a mica window. From the β-activity found, the U content is found by means of the standard curve.

Determination of Io. After the measurements have been made on the β-counter, the precipitate is transferred to an agate mortar in which it is ground under acetone. The fine suspension in acetone is evaporated on a weighed disc in an apparatus for evaporating under a lamp. The disc plus precipitate are weighed, and the α-activity of the latter measured. The Io content is expressed in impulses/ minute or in uranium units by comparing with a standard sample prepared in a fine layer.

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[*] If, during the repeated treatment, the iron should be removed completely (a dilute hydrochloric acid solution of iron is practically colorless), 10 mg of $FeCl_3$ should be added before precipitation with NH_4OH.

[**] When the uranium content is 1×10^{-4} %, the sample taken should not be less than 10-15 g. When such a sample is taken, it is convenient to deal in parallel, with say 3 lots of 5 g each, all three lots being combined before determination of uranium, Consequently, after the Th determination, the contents of all three colorimeter tubes are poured into one beaker and the Th isotopes precipitated on iron in the beaker as usual.

Preparation of a Standard Curve for Determination of U According to the β-count for UX_1. 100, 200, 300, 400, and 500 γ of radiochemically pure uranium together with the equilibrium amount of $UX_1 - UX_2$ is precipitated with NH_4OH (free from CO_2). $FeCl_3$ added in amounts of 2 mg in each case is used as the carrier. The precipitates obtained are dried and calcined and their activity measured on a β-counter. A calibration curve relating the value of the measured β-activity to uranium content is then constructed.

In conclusion we should like to thank V. I. Kuznetsov for his advice on determination of thorium by means of thoron, and also for valuable advice which enabled us to eliminate a number of drawbacks in the method developed.

SUMMARY

1. A technique has been developed for the determination of uranium, thorium, and ionium in sea silt on one sample aliquot.

2. Completeness of separation and the radiochemical purity of the isotopes were checked by means of indicators.

3. The method has been tried out on samples of sea silt, and also on rocks, ores, and minerals.

4. The method is applicable to materials containing 5×10^{-5} to $x \cdot 10^{-4}$ % of thorium, 10^{-4} to 70 % of uranium, and for contents of ionium of $x \cdot 10^{-4}$ % (in uranium units).

The absolute experimental error does not exceed 10-15 %.

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A SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF LEAD, TIN, CADMIUM, ANTIMONY AND BISMUTH IN METALLIC RHENIUM

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Production of metallic rhenium with a high degree of purity requires development of methods for determining a number of impurities in it, the presence of which affects the most important physicochemical properties of the metal. The most important impurities are bismuth, lead, tin, antimony, and cadmium. The content of each of these metals in metallic rhenium should not exceed 1×10^{-4} %. In the literature available to us, we were unable to find references to methods devoted to the determination of these metals at such a concentration in rhenium.

The insufficient sensitivity of the spectrographic determination of these metals, and the complexity of the spectrum of the main component complicated the application of direct spectrographic determination for solving the problem posed, and necessitated the use of combined analytical techniques, which include preliminary concentration of the impurities to be determined. In the work described in the present article, several methods of solving these problems were tested, these included:

1. A physical enrichment method, based on fractional separation of the elements — removal of impurities from the main component on an evaporating setup [1-3].

2. Chemical concentration of the impurities by selective separation of Pb, Bi, Sb, Sn, and Cd during coprecipitation with hydrogen sulfide [4].

3. Chemical enrichment of the impurities by removal of the main component by precipitation with thallium acetate in an acetic acid medium, with subsequent concentration of the impurities on beryllium oxide.

4. Physical enrichment of the impurities by careful distillation of rhenium from the sample at 200-300°, the impurities being transferred to a new base — carbon powder.

Application of the first two methods came up against difficulties, connected in the first instance with difficulties in preparing standards for work with metallic rhenium, while in the second case difficulties arose as a result of considerable trapping of rhenium as well as the impurities during coprecipitation with hydrogen sulfide. More satisfactory results were obtained on using the last two methods of enriching the impurities.

1. Chemicospectrographic Determination of Impurities in Metallic Rhenium by Separation of the Latter with Thallium Acetate in Acetic Acid Media

Rhenic acid $HReO_4$ forms salts which are sparingly soluble in water with a number of cations. One of these salts is thallium rhenate $TlReO_4$; the solubility of this salt at 10° is 0.0085 g/liter, while at 26° its solubility is 0.016 g/liter. The solubility can be decreased by addition of acetic acid to the solution.

This property of rhenium can be used as a basis for developing a chemicospectrographic technique for the determination of impurities in the basic metal. The method consists of the following stages: a) chemical separation of the metal — i.e., removal of the main component from its impurities; b) concentration of the impurities on beryllium oxide followed by subsequent analysis of the concentrate.

a) Chemical Preparation of Samples for Spectrographic Analysis

Rhenium was separated chemically from its impurities as follows. 1 g of metallic rhenium was dissolved in 10 ml of diluted (1 : 1) nitric acid in a quartz beaker. Acetic acid and a solution of thallous acetate or nitrate were then added to the beaker. A white crystalline precipitate of thallium perrhenate was thereupon formed. As tests showed, it is possible in this way to realize fairly complete precipitation of rhenium, and this reaction, as is well known [5, 6], can be succesfully used for the quantitative determination of small amounts of rhenium. After standing for a reasonable time (not too long) the precipitate was filtered, and then washed with glacial acetic acid and 96° ethanol. In order to transfer the impurities onto a new base, the filtrate plus wash liquors were evaporated in a quartz basin on a water bath to a volume of approximately 10 ml. A solution of purified beryllium nitrate $Be(NO_3)_2$ was then added, the amount of the latter being determined by the normality of the solution and by the required enrichment coefficient. Pure beryllium nitrate was prepared after purification of beryllium oxide by extraction of the basic acetate $Be_4O(CH_3COO)_6$ with chloroform. 3-6 ml of ammonia NH_4OH was then added to the extract in the quartz basin. The white paste formed was then dried and finally calcined at 400-500°. The concentrated impurities from the sample prepared in this way, were then ground in an agate mortar, weighed, and analyzed spectrographically.

Spectrographic Determination of the Impurities

A dc arc was used for spectrographic determination of the impurities. The arc was fed from a mercury rectifier with a voltage of 250 volts. Standards were prepared on the basis of pure beryllium oxide using a method similar to that for preparation of the concentrates. The impurities were added in the form of 0.01 % solutions of the nitrates.

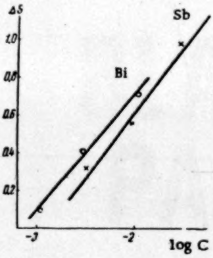

Fig. 1. Calibration curves for determination of bismuth and antimony.

The spectra of the standards and concentrates were photographed on one plate, using the ISP-22 quartz spectrograph, with a one-condenser system of illumination ($f_{\text{condenser}}$ = 75 mm). The plates had a sensitivity of 2 GOST units; the slit width was 10 μ, the interelectrode distance was 3 mm, the current strength was 10 amperes, while exposure time was 1 minute. The test sample, weighing 20 mg, was placed in the crater of the lower electrode (anode), the depth of the crater being 5 mm, while its diameter was 3.5 mm. The upper electrode (cathode) was sharpened to a cone.

The following analytical lines of the test impurities were used: Sb — 2598.06; Bi — 3067.72; Cd — 2288.02 A. Calibration curves were constructed within the coordinates ΔS, log c, where ΔS is the difference in blackening of the analytical lines and the background; while c is the concentration expressed in percent. As an example, we have shown on Fig. 1 the calibration curves for bismuth and anitmony. The calibration curve for cadmium has a similar shape.

During the preliminary operations of preparing the concentrates, impurities may get in, mainly with the reagents, and partial losses of the impurities to be determined may occur, chiefly, during filtration of the precipitate. In order to determine the magnitude of such losses, radioactive indicators were used to study the separation of rhenium from its impurities.

The radioactive isotopes used for this purpose are given in Table 1.

The isotopes listed in Table 1 were obtained by neutron bombardment of spectrographically pure Sb, Sn, and Bi metals, Cd oxide, and lead acetate. The indicators, after they had been dissolved, were added to the acetic acid solution of rhenic acid. Rhenium was precipitated with thallium acetate, and the precipitate checked for purity. Experiments showed that thallium perrhenate does not trap Bi, Cd and Sb, which remain practically completely in the filtrate. Tin is partially trapped by the precipitate (up to 30%); lead is completely coprecipitated.

The purity of the reagents used and the absence of appreciable contamination during the preliminary operations were checked in blank tests. The solution of thallium acetate was prepared from spectrographically pure metallic thallium.

The technique described permits determination of Sb, Cd, and Bi with a sensitivity of 1×10^{-4} % and higher, for enrichment coefficients equal to and greater than 20.

TABLE 1

Element	Mass number	Half-life period	Nature of radiation	Radiation energy, in MeV		Reactions used for formation of the isotope
				β-particles	γ-rays	
Sb^{51}	122	2.8 days	β^-, γ	1.36	0.568	Sb(n, γ)
				1.94	0.68; 1.25	
Cd^{48}	115	2.2 days	β^-, γ	0.6	0.335	Cd(n, γ)
				1.12	0.337	
					0.3337	
Bi^{83}	210	5 days	β^-	1.17	Neg.	Bi(n, γ)
Pb^{82}	209	3.32 hours	β^-	0.64	"	Pb(n, γ)
Sn^{50}	121	1.1 days	β^-	0.385	"	Sn(n, γ)
	125	9 days		2.6	"	
		10 days	β^-	1.8	"	Sn(n, γ)

The reproducibility of the quantitative determination of impurities in rhenium amounts to 15-20 % when this technique is used. The drawback of this technique is that it does not permit determination of impurities such as Pb and Sn which are often met in metallic rhenium. It also requires the use of a considerable amount of reagents.

2. Spectrographic Determination of Impurities in Metallic Rhenium After Removal of the Latter by Distillation

Rhenium oxide Re_2O_7 distills at 200-300°; the impurities are concentrated.

Preparation of concentrates involved the following operations. In a quartz beaker, 1 g of metallic rhenium was dissolved in a mixture of 2-3 ml of twice distilled nitric acid and 7-8 ml of water, by slight warming. The solution was evaporated to 4-5 ml and placed, together with a weighed aliquot of carbon powder (100 mg), in a platinum or quartz crucible. The mixture obtained was placed on a hot plate and the rhenium carefully distilled off, the residue was then calcined in a muffle at 400-500° for 10-15 minutes. The concentrate prepared in this way was then analyzed spectrographically. A dc arc with carbon electrodes (6 mm) was used as an excitation source for the spectrographic determination. The arc was supplied from a mercury rectifier operating at a voltage of 250 volts.

An ISP-22 spectrograph with a one-condenser system of illuminating the slit ($f_{condenser}$ = 75 mm) was used, in order to cut down on loss of light.

The optimum conditions for carrying out the analysis were as follows: slit width 10 μ; inter-electrode distance 3 mm; the depth of the crater in the lower electrode into which the sample was fed was 5 mm while its diameter was 3.5 mm; the upper electrode was sharpened to a cone. The standards were prepared from carbon powder which had been calcined in the arc; this powder contained the following amounts of all five impurities: I) $3 \cdot 10^{-3}$ %; II) $1 \cdot 10^{-3}$ %; III) $3 \cdot 10^{-4}$ %; IV) $1 \cdot 10^{-4}$ %.

For preparation of standards with the highest content of impurities, the latter were introduced by moistening the carbon powder with the calculated amount of 0.01 % solutions of the nitrates of Pb, Sn, Sb, Bi, and Cd; the carbon powder was then dried and calcined at 400-500° in the course of 10-15 minutes. The remaining standards were prepared by diluting the more concentrated standards. The concentrated impurities from samples and standards (weights of 20 mg) were evaporated from the crater in the lower electrode under identical conditions. The spectra were registered on reproducing plates with a sensitivity of 2 GOST units. They were developed in a D-19 developer for 4 minutes.

The analytical lines used were the following: Cd 2288.02; Sb 2598.06; Pb 2833.07; Sn 2839.99; Bi 3067.72.

Sb and Bi lines may be masked by the background from Fe lines. Experiments showed, however, that the Fe content of pure industrial samples of rhenium does not interfere when working with the analytical lines chosen for the test impurities.

Calibration curves (Figs. 2 and 3) were constructed within the coordinates ΔS, log c, where ΔS is the difference between the blackening of the lines and the background, while c is the concentration (in %).

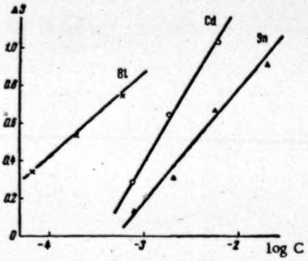

Fig. 2. Calibration curves for determination of bismuth, cadmium, and lead.

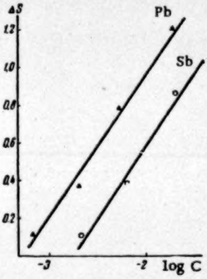

Fig. 3. Calibration curves for determination of lead and antimony.

The technique described permits determination of impurities at the following concentrations 2×10^{-4} %Sb, and 1×10^{-4} % of Pb, Sn, Cd, and Bi. Sensitivity of determination of the latter elements can be made even higher. Reproducibility of the determinations is 15-20 %.

TABLE 2

Sample Number	Content, in %				Content, in %			
	$k-1$	$k-5$	$k-10$	Mean value	$k-1$	$k-5$	$k-10$	Mean value
1	$4.2 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$9.7 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$
2	$3.5 \cdot 10^{-3}$	$2.4 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$3.4 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$	$3.2 \cdot 10^{-3}$

The method was checked, and its reliability established, by means of results obtained during analysis carried out in three series of independent experiments. In the first series of experiments, the same sample was analyzed at various degrees of enrichment (by varying the ratio of sample to carbon powder). The agreement between the results testified to the absence of any appreciable increase of impurities in the main component. In the second series, an industrial sample of rhenium was analyzed by the two techniques described above, as well as by a third — experiments were carried out in which a known weight was added and then this amount determined analytically. The results of these experiments are given in Tables 2, 3, and 4.

TABLE 3

Impurity	By the method in which rhenium is precipitated, in %	Method in which rhenium is distilled, in %
Sb	$2.8 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$
Bi	$2.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$
Cd	$9.1 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$

TABLE 4

Impurity	First problem		Second problem		Third problem	
	Added	Found	Added	Found	Added	Found
Pb	$1 \cdot 10^{-3}$	$8.8 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$9.6 \cdot 10^{-5}$
Sn	$1.4 \cdot 10^{-3}$	$1{,}7 \cdot 10^{-3}$	$7{,}3 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	$5.3 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$
Sb	$1 \cdot 10^{-3}$	$9\ 1 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$3{,}4 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
Bi	$1 \cdot 10^{-3}$	$9{,}2 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$7.9 \cdot 10^{-5}$
Cd	$1 \cdot 10^{-3}$	$1{,}3 \cdot 10^{-3}$	$3 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$8.6 \cdot 10^{-5}$

The results given in Tables 2, 3, and 4 show that there is no systematic loss in the impurity metals which appreciably affect the analytical results, while the mean arithmetic error does not exceed 15-20 %.

The method in which rhenium is evaporated from the sample while the impurities are concentrated on carbon powder, could probably be used, without any essential modifications, for the determination of several other impurities present in metallic rhenium, such as Fe, Mo, Ca, Mg, etc.

In conclusion, we should like to thank E. E. Vainshtein for valuable advice in connection with the fulfilment of the work.

SUMMARY

1. A chemicospectropgraphic method has been developed for determining Cd, Bi, and Sb, in metallic rhenium, the sensitivity of the method being 1 x 10^{-4} %, while the accuracy is 15-20 %.

2. A spectrographic method is suggested for determination of Pb, Sn, Cd, Bi, and Sb in metallic rhenium, in which the main component is removed by evaporation. The sensitivity of this method is 2 x 10^{-4} % in the case of Sb, while it is 1 x 10^{-4} % for Pb, Sn, Cd, and Bi; the accuracy is 15-20 %.

3. A comparison of the two methods for determining the Sb, Bi, and Cd of metallic rhenium, has shown that there is satisfactory agreement between the results obtained by both methods.

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KINETIC METHODS OF QUANTITATIVE ANALYSIS

COMMUNICATION 4. DETERMINATION OF SMALL AMOUNTS OF TUNGSTEN*

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Quantitative determination of a number of elements can be realized by making use of their catalytic action on reactions whose rate is comparatively slow and is convenient for measurement.

Oxidation of iodide by hydrogen peroxide in acid media at room temperature proceeds very slowly in the

$$H_2O_2 + 2I_2^- + 2H^+ = I_2 + 2H_2O \qquad (1)$$

absence of catalysts [1, 2]. It has been established that the reaction rate increases in the presence of traces of compounds of sexivalent molybdenum and tungsten, as well as of traces of iron, uranium, and chromium [3, 4]. Catalysis of reaction (1) by molybdate has been used for developing a method for its determination [5]; we have used this reaction for developing a method for the quantitative determination of small amounts of tungsten.

EXPERIMENTAL

The stock solutions used were 0.0100 M H_2O_2, and 0.00500 M KI, the concentrations in solution after mixing being: KI = 50.0×10^{-4} mole/liter; $H_2O_2 = 1.00 \times 10^{-3}$ mole/liter. All the solutions were prepared from chemically pure reagents, the concentrations of the solutions being established by standard methods. In view of the absence of methods for the determination of small concentrations of tungsten, the stock solution of tungstate was prepared by accurate dilution of 0.02500 M of molybdate, the tungsten concentration of the original solution being determined gravimetrically.

Hydrochloric acid, potassium iodide, and tungstate solutions, as well as water and starch, were introduced into a 50 ml standard flask, the whole thoroughly mixed, and the volume made up to the mark with water and the final solution again mixed. When hydrogen peroxide was added the stop watch was started. The concentrations of the reagents in the solution after mixing were: KI = 5.00×10^{-4} mole/liter; $H_2O_2 = 1.00 \times 10^{-3}$ mole/liter; HCl = 0.100 mole/liter; tungstate from 5.00×10^{-8} - 5.00×10^{-7} mole/liter. The solution was then introduced into the cell of an FEK-M photoelectrocolorimeter, and the optical density of the solution measured after various time intervals using a KS-14 light filter. All determinations were made at 24-25°.

On the basis of the results obtained a curve for optical density against time was plotted. These curves proved to be straight lines (Fig. 1). The tangent of the slope of the straight line determines the rate of the oxidation reaction in each case, and, consequently, other conditions being equal, determines the catalyst (tungstate) concentration.

From the experimental results a curve was constructed relating the value of the tangent of the slopes of the straight lines and tungsten concentration — all the points again lie on a straight line (Fig. 2). This curve can be used as a calibration curve by means of which it is possible to determine tungstate concentration.

In further experiments, tungstate was determined as follows: the reaction mixture described above was made up, only in this case, instead of the standard solution of tungstate, the test solution was used and density measurements carried out on the FEK-M apparatus, a curve was then drawn relating optical density to time, the slope of the straight line obtained was determined. Finally, using the calibration curve (Fig. 2), the concentration of tungstate in the test solution was determined.

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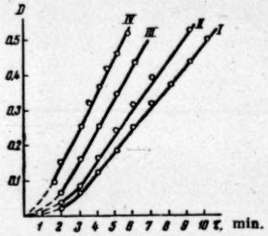

Fig. 1. Changes in optical density in the system KI$-H_2O_2-Na_2WO_4-$HCl$-$starch$-$water.
Tungstate concentration:
I) 5.0 x 10^{-8} mole/liter; II) 1.0 x 10^{-7} mole/liter; III) 1.5 x 10^{-7} mole/liter; IV) 2.0 x 10^{-7} mole/liter.

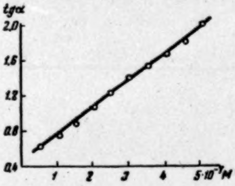

Fig. 2. Relation between rate of reaction (1) and tungstate concentration.

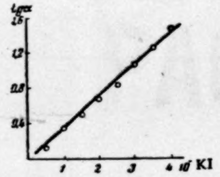

Fig. 3. Relation between rate of reaction (1) and iodide concentration.

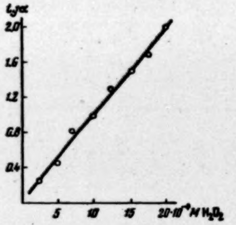

Fig. 4. Relation between rate of reaction (1) and hydrogen peroxide concentration.

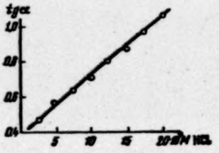

Fig. 5. Relation between rate of reaction (1) and hydrochloric acid concentration.

TABLE 1

Evaluation of the Reproducibility of the Method
(2.00 x 10^{-7} mole/liter of tungstate taken)

Tungstate found, in mole/liter	Deviation, in %
$2.15 \cdot 10^{-7}$	+7.5
$1.89 \cdot 10^{-7}$	−5.5
$2.00 \cdot 10^{-7}$	0
$1.82 \cdot 10^{-7}$	−9
$2.15 \cdot 10^{-7}$	+7.5
$2.05 \cdot 10^{-7}$	+2.5

Next we studied the relation between the rate of the catalytic reaction and iodide concentration. This was carried out by adding variable amounts of KI solution to a reaction mixture containing 1.00 x 10^{-3} mole/liter of

H_2O_2; 0.100 mole/liter HCl, and 5.00 x 10^{-7} mole/liter of Na_2WO_4, and the reaction rate then determined. The relation between reaction rate and iodide concentration is shown on Fig. 3. In the same way, the relation between reaction rate and hydrogen peroxide concentration was studied (Fig. 4), as well as the relation between reaction rate and the acid concentration of the solution (Fig. 5).

In order to evaluate the reproducibility of the method, 6 solutions of sodium tungstate containing the same amount of this salt were prepared from pure solutions of tungstate, their concentrations were then determined kinetically as described above. The results obtained are given in Table 1.

The mean square deviation amounts to ± 6%.

TABLE 2

Effect of Other (Foreign) Ions on Tungsten Determination (tungsten concentration 1.00 x 10^{-7} mole/liter)

Other ion	Concentration of the other ion, in g ion/liter	Ratio of concentration of other ion to tungsten ions	Slope of the straight line	Other ion	Concentration of the other ion, in g·ion/liter	Ratio of concentration of other ion to tungsten ions	Slope of the straight line
—	—	—	$0.77 \cdot 10^{-1}$	Cd^{2+}	$5.0 \cdot 10^{-5}$	$5 \cdot 10^{2}$	$0.64 \cdot 10^{-1}$
Ca^{2+}	0.10	10^{6}	$0.78 \cdot 10^{-1}$	Hg^{2+}	$5.0 \cdot 10^{-5}$	$5 \cdot 10^{2}$	$0.63 \cdot 10^{-1}$
Mg^{2+}	0.20	$2 \cdot 10^{6}$	$0.81 \cdot 10^{-1}$	Cu^{2+}	$1.0 \cdot 10^{-3}$	10^{4}	$0.83 \cdot 10^{-1}$
Al^{3+}	0.10	10^{6}	$0.80 \cdot 10^{-1}$	AsO_4^{3-}	$1.0 \cdot 10^{-4}$	10^{3}	0
Zn^{2+}	0.10	10^{6}	$0.79 \cdot 10^{-1}$	SiO_3^{2-}	$1.0 \cdot 10^{-4}$	10^{3}	0
Ni^{2+}	0.10	10^{6}	$0.81 \cdot 10^{-1}$	F^-	$1.0 \cdot 10^{-4}$	10^{3}	0
Co^{2+}	0.10	10^{6}	$0.80 \cdot 10^{-1}$	Citrate	$1.0 \cdot 10^{-4}$	10^{3}	0
Mn^{2+}	0.10	10^{6}	$0.80 \cdot 10^{-1}$	Tartrate	$1.0 \cdot 10^{-4}$	10^{3}	0
Na^+	1.0	10^{7}	$0.80 \cdot 10^{-1}$	Oxalate	$1.0 \cdot 10^{-4}$	10^{3}	0
Fe^{3+}	$3.0 \cdot 10^{-5}$	$3 \cdot 10^{2}$	$0.82 \cdot 10^{-1}$	H_3PO_4	$1.0 \cdot 10^{-4}$	10^{3}	$0.69 \cdot 10^{-1}$
Pb^{2+}	$3.0 \cdot 10^{-5}$	$3 \cdot 10^{2}$	$0.75 \cdot 10^{-1}$				

In order to establish the effect of the presence of other ions on the rate of the catalytic reaction (and, consequently, on the kinetic determination of tungsten), various salts were introduced into the reaction mixture. The concentration of the other ion was several thousand times the concentration of the tungsten. The results obtained are given in Table 2.

TABLE 3

Solubility of H_2WO_4 in 1 N HCl

Experiment number	Solubility, in mole/liter x 10^{-4}	Deviation from the mean, x 10^{-4}
1	1.00	-0.01
2	1.09	+0.08
3	0.88	-0.13
4	0.96	-0.05
5	1.13	+0.12
Mean	$1.01 \cdot 10^{-7}$	

Mean value of the solubility (1 ± 0.1) x 10^{-4} mole/liter.

TABLE 4

Solubility of Hg_2WO_4 in Water

Experiment number	Solubility, in mole/liter x 10^{-4}	Deviation from the mean, x 10^{-4}
1	2.16	-0.04
2	2.28	+0.08
3	2.10	-0.10
4	2.14	-0.06
5	2.29	+0.09
6	2.23	+0.03
Mean	$2.20 \cdot 10^{-6}$	+0.03

Mean value of the solubility (2.2 ± 0.2) x 10^{-4} mole/liter.

Since it is possible to determine negligibly small amounts of tungsten by the kinetic method, we decided to use this method for determining the solubility of tungstic acid and mercurous tungstate. These compounds are the main forms in which tungsten is precipitated during its gravimetric determination; the results reported in the literature for the solubility of these compounds are few and contradictory. Thus, Rabinovich and Kargin [6] give a value of 3×10^{-5} mole/liter for the solubility of H_2WO_4. Schumb and Hartford [7] give a value of 33×10^{-4} mole/liter; there are no available reliable results for mercurous tungstate.

Tungstic acid forms colloidal solutions in water, accordingly, we determined its solubility in 1 N hydrochloric acid. H_2WO_4 and Hg_2WO_4 were prepared from the chemically pure reagents, the WO_3 content was determined by calcining an aliquot of the material, dried to constant weight at 120°, in a muffle at 730°. All determinations were carried out in apparatus thermostatted at 25°.

An aliquot of test material was placed in a 500 ml flask which was provided with a stirrer.The solvent was then added. The vessel was kept in a thermostat at 25 ± 0.05° for several hours. Samples of the solution were taken periodically and their tungsten content determined kinetically. The results obtained are given in Tables 3 and 4.

DISCUSSION OF RESULTS

On the basis of the experimental results we suggest the following equation for the rate of the catalytic reaction

$$d[I_2]/d\tau = \varkappa \cdot c_{I^-} \cdot c_{H_2O_2} \cdot c_W, \qquad (2)$$

where $\varkappa$ is the catalytic coefficient, while c_I, $c_{H_2O_2}$, and c_W are the concentrations of iodide, hydrogen peroxide, and tungstate respectively. The catalytic coefficient depends on acidity. This, apparently, may be explained by the fact that it is the cationic forms of tungsten which are catalytically active, and increasing the acid concentration leads to an increase in the concentration of these cationic forms, and, possibly, alters their structure. When the acid concentration is 0.1 M, the catalytic coefficient as evaluated by equation (2) is 1.0×10^8 (time in minutes, concentrations in mole/liter).

On the basis of theoretical considerations advanced previously [8], it is possible to evaluate the minimum concentration of tungsten which can be detected by this method. In order to carry out this calculation, it is necessary to know the rate of the uncatalyzed reaction. Under the conditions we used, this value, according to published results [2] is equal to 1.89, from which

$$c_{W_{\min}} \geq 0.1 \frac{k}{\varkappa} \approx 2 \cdot 10^{-9} \text{ mole/liter.}$$

Consequently, the method we suggest is more sensitive than all methods known hitherto for determination of tungsten.

Tungsten can be determined by the method developed in the presence of a number of other elements. Calcium, magnesium, aluminum, zinc, nickel, cobalt, and manganese do not essentially affect the reaction rate at the concentrations of these metals studied. Copper accelerates liberation of iodine somewhat, presumably, as the result of the reaction $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$.

Lead, mercury, and cadmium slow down the reaction, since they form complex ions with the iodide, thereby lowering the effective iodide concentration. Phosphates slow down the reaction, while fluorides, citrates, tartrates, oxalate, arsenate, and silicate, in the concentrations studied, completely suppress the catalytic action of tungsten.

SUMMARY

A new, highly sensitive method has been developed for the quantitative determination of tungsten, which is based on using the catalytic effect of tungsten on the oxidation of iodide by hydrogen peroxide.

It has been found that the solubility of tungstic acid in 1 N hydrochloric acid is $(1.0 \pm 0.1) \times 10^{-4}$ mole/liter, while that of mercurous tungstate in water is $(2.2 \pm 0.2) \times 10^{-4}$ mole/liter.

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SPECTROCHEMICAL DETERMINATION OF PLATINUM AND PALLADIUM IN URANIUM

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During determination of small amounts of the platinum group elements in uranium, normal methods of spectrographic analysis which are connected with excitation of the spectra of the test materials in an arc or spark source of light, do not lead to success. Consequently, it is necessary to use some chemical method of enrichment of the samples.

During determination of noble metals in ores, some authors [1-3] have separated the metals from the samples by cupellation and crucible fusion with lead. During analysis of pure samples of uranium, however, the problem can be solved in a simpler fashion, namely by precipitation of platinum group elements in the form of their sulfides by means of hydrogen sulfide. When this is done, practically all the uranium remains in solution.

In order to attain analytical sensitivity of the order of about 10^{-4} %, it is necessary to separate 1 μg of Pt and Pd from a solution containing at least 1 g uranium. Copper was chosen as a carrier, since this metal is known to be a good collector for coprecipitation of platinum.* Copper was added to the original sample in the form of a solution of its sulfate (0.1 mg of Cu per g of uranium). Precipitation was carried out from hot 2N solutions of H_2SO_4. The sulfides obtained were dissolved in aqua regia and placed on the end surface of a carbon electrode which had been moistened beforehand with a solution of polystyrene in benzene. Completeness of precipitation of platinum and palladium was checked spectroscopically. It was established that during the spectrographic determination of platinum and palladium in synthetic mixtures (10^{-4} - 10^{-2} % of Pt and Pd in uranium), a linear relation can be obtained between the blackening of the analytical lines and the logarithm of the concentration of the test element.

This simple operation of coprecipitating the sulfides of platinum and palladium with copper made it possible to free the test metals practically completely from uranium. Even the last lines of uranium were absent in the spectra of the concentrates obtained. The poor copper lines in the spectra did not interfere with the spectroscopic determination of platinum and palladium. Spectrographic analysis of the concentrate was carried out in a condensed spark (an IG-2 generator, C = 0.012 μF, L = 0.15 mH, inter-electrode distance 2 mm, exposure 10 seconds). The spectra were photographed on an apparatus with average dispersion (ISP - 22 or Q - 24). "Spectrographic, Type II" plates were used.

Considerable attention was devoted to the question of standardization during development of the method. In the first experiments, attempts were made to use copper as the reference element. This simple and convenient method of introducing an internal standard, however, could not be used, since it led to distortion of the analytical results during determination of platinum and palladium in uranium samples contaminated with copper. Choice of another element whose sulfide would also be precipitated quantitatively with copper, proved difficult; accordingly, taking into account the good reproducibility of the enrichment process, we decided to introduce the element to be used as an internal standard, into the concentrate after enrichment, and not to the original sample. The reference element finally chosen was gold which was introduced in the form of a 0.01 % solution of $AuCl_3$, the amount added being such that 2 μg of metallic gold was finally found on the electrode. This same amount of gold was placed on the electrode when the standard mixtures were used, the latter having been prepared from solutions of the pure salts of platinum, palladium, and copper. Analysis was subsequently carried out by the three standards method. Table 1 contains the analytical lines and reference lines used for determination of platinum and palladium. These pairs of lines are sufficiently homogeneous, while the somewhat large distance in the wave lengths of the lines of platinum and palladium used does not play a special part in the comparatively low accuracy necessary for determination of small concentrations.

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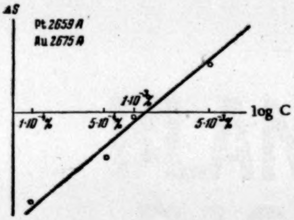
* The authors wish to thank O. E. Zviagintsev for pointing this out to them.

TABLE 1

Analytical lines, in A	Reference lines, in A	Concentration range for determination of Pt and Pd in uranium, in %
Pt I 2659.45	Au I 2675.95	$1 \cdot 10^{-4} - 3 \cdot 10^{-3}$
Pt I 3421.24	Au I 3122.78	$3 \cdot 10^{-5} - 1 \cdot 10^{-3}$

The use of such a standardization technique reduces the errors which arise during the photography of the spectra, and simplifies experimental procedure. The only errors which remain to be controlled are those which occur during precipitation of the sulfides of the test elements. Numerous tests showed, however, that these errors are very small. The probable error of a single determination of platinum in uranium, for a concentration of about 10^{-4} % of platinum in the latter, proved to be less than 20 %. This over-all error was calculated on the basis of more than 30 measurements, and is made up of errors connected with enrichment operations, standardization errors, and errors arising during spectrographic analysis of the concentrates. On the diagram is shown a calibration curve for determination of platinum in uranium, with a sensitivity of $1 \cdot 10^{-4}$ %. Under the same conditions, palladium can be determined with a sensitivity of $3 \cdot 10^{-5}$ %. The analytical sensitivity for determination of these elements can be increased by increasing the weight of the original uranium taken for analysis, the normal weight of the latter normally used being 1 g.



Calibration curve for determination of Pt in U_3O_8

This method can be used for the determination of platinum and palladium in other metals. The necessary condition for its application is that the main component of the test sample is not precipitated by hydrogen sulfide. In particular, we studied the possibility of determining platinum in mixtures of the rare earths. On passing hydrogen sulfide through a solution of the sulfates of the rare earths, the latter remain in solution, while platinum sulfide is precipitated with the carrier (Cu). The analytical sensitivity proved to be somewhat lower than for the determination of platinum in uranium, since, as a result of the low solubility of the sulfates of the rare earths, it was necessary to use a smaller amount of test sample for analysis.

The authors wish to thank G. G. Kund, and P. P. Iakimova for carrying out the control tests.

SUMMARY

A method is suggested for the determination of small amounts of platinum and palladium in uranium. After platinum and palladium have been coprecipitated with copper as the sulfides, the former are determined spectrographically. The method permits quantitative determination of 10^{-4} % of Pt and $3 \cdot 10^{-5}$ % of Pd in uranium.

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A NEW METHOD OF DETERMINING TELLURIUM

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The most important methods of determining tellurium and selenium are based on their reduction to the elemental state in acid solutions, with subsequent weighing of the elemental forms.[1]. Sulfur dioxide gas, hydroxylamine hydrochloride, hydrazine hydrochloride or sulfate, and sodium sulfite have been used as reducing agents.

Titrimetric methods of determining tellurium and selenium are based on the oxidation of tellurites and selenites to tellurates and selenates respectively by strong oxidizing agents [2, 3]. Photometric, polarographic, and other methods are also known for the determination of tellurium and selenium.

We have found that tellurites and selenites, as well as tellurates and selenates, are reduced to the elemental state on boiling with lactose at pH of 10-11. Tellurium, after 5-10 minutes boiling, is completely converted into a readily filtrable precipitate.

The rate of reduction by lactose depends to a very large extent on the temperature. In the cold, lactose does not reduce selenium and tellurium, even in alkali solutions, while on boiling, this process is very rapid. Acid solutions of tellurites are not reduced by lactose. The amount of free alkali added for this reduction to occur, affects the nature of the precipitate and the nature of the reduction process itself. Thus, when there is insufficient alkali, the reduction is held up to a considerable extent, and there is formed a fine precipitate which is difficult to filter. When a large amount of alkali is present, on the other hand, tellurium is not deposited quantitatively. When the amount of alkali is sufficient, after boiling, the color of the solution is a light cherry-red, while when insufficient alkali is present, the solution has a greenish cherry-red color, and when excess alkali is present, the color is a dark cherry-red with a raspberry tinge.

After reduction of tellurites with lactose in a weakly alkaline medium, the determination is finished either gravimetrically or titrimetrically. The method is applicable to the determination of tellurium in its alloys with antimony.

A Gravimetric Method for the Determination of Tellurium

0.0200-0.0300 g of finely ground Kahlbaum tellurium was treated in a closed 100-150 ml conical flask with 10 ml of HNO_3 1 : 1, to which has been added a small amount of $NaNO_2$ crystals. The tellurium is first treated in the cold, and then heated. After the material had dissolved and nitrogen oxides had been removed by boiling for a short time, the solution obtained was neutralized with 40 % sodium hydroxide. When neutralization was almost complete, a few drops of phenolphthalein was added and neutralization completed by dropwise addition of the alkali to the pink color of the indicator. 6-8 drops of the 40 % solution of sodium hydroxide was added in excess, and then 5 ml of a 20 % lactose solution added, the mixture was diluted with water to 50-60 ml and the whole boiled for 5-10 minutes. After boiling, the solution was carefully mixed by swirling the flask, and then allowed to stand. When the color of the supernatant solution above the precipitate was a cherry red, the solution was allowed to get cold and was then filtered through a No. 4 tared glass crucible. The precipitate was washed 3-4 times by decantation with hot water, and then washed 4-5 times on the filter in order to remove NO_3^- ions. The precipitate was then washed 2-3 times with small portions of alcohol to remove water, and finally dried at 105° to constant weight. Results of these gravimetric determinations are given in Table 1.

Titrimetric Determination of Tellurium

The most important titrimetric methods of determining tellurium are based on the following reactions [2,3]:

$$5TeO_3^{2-} + 2MnO_4^- + 6H^+ = 5TeO_4^{2-} + 2Mn^{2+} + 3H_2O;$$
$$3TeO_3^{2-} + Cr_2O_7^{3-} + 8H^+ = 3TeO_4^{2-} + 2Cr^{2+} + 4H_2O.$$

The equivalent weight of tellurium is 63.85.

We turned our attention to the fact that freshly precipitated tellurium dissolves fairly readily in an acidified solution of potassium dichromate, during which tellurium is oxidized to telluric acid:

$$Te + Cr_2O_7^{2-} + 6H^+ = TeO_4^{2-} + 2Cr^{3+} + 3H_2O.$$

We used this fact for the quantitative determination of tellurium. The equivalent weight of tellurium in this reaction is 21.27. It is best to use sulfuric acid rather than hydrochloric acid for acidifying the dichromate solution, since on heating the hydrochloric acid, it reduces the sexivalent tellurium formed to the quadrivalent state.

TABLE 1

Tellurium taken, in g	Tellurium found, in g	Difference, in g.
0.0304	0.0304	0.0000
0.0221	0.0220	- 0.0001
0.0246	0.0243	- 0.0003
0.0286	0.0286	0.0000
0.0256	0.0258	+ 0.0002

TABLE 2

Tellurium taken, in g	Tellurium found, in g	Difference, in g
0.0274	0.0272	-0.0002
0.0232	0.0229	-0.0003
0.0248	0.0248	0.0000
0.0250	0.0249	-0.0001
0.0276	0.0274	-0.0002

Tellurium was determined as follows. The aliquot of tellurium was treated in exactly the same way as during the gravimetric determination. The cooled mixture was filtered through a plug of glass wool and special asbestos of the type used for Gooch crucibles. This plug was prepared as follows: a thin layer of glass wool was placed in the stem of an ordinary analytical funnel, this was followed by a layer of asbestos which was then packed so that the flow rate of water from the funnel packed in this way was one drop per second. The precipitate was washed with a hot, 2 % solution of sodium sulfate, first by decantation 3-4 times, and then washed on the filter itself 4-5 times. The washed precipitate was washed off the funnel (together with the asbestos) into the same flask, 20 ml of 0.1 N $K_2Cr_2O_7$ and 10 ml of 4 N H_2SO_4 were then poured through the funnel into the same flask into which the precipitate had been washed. In this way the precipitate sticking to the funnel was dissolved. It was found advisable to rub the inner surface of the funnel with a glass rod, so that the precipitate can be broken up and thereby can be dissolved more readily. When the precipitate of tellurium sticking to the funnel had been completely dissolved, it was washed a few times with water and then stored. Heating the mixture to 50-60° favored more rapid dissolving of the precipitate; it was sufficient to mix and break up the larger particles of tellurium with a glass rod. When the precipitate had dissolved completely, 15-20 ml of a standard solution of Mohr's salt was added to the cooled mixture, followed by 5 ml of H_3PO_4 1 : 1, 10-15 ml of 2 N HCl, and 3 drops of a 1 % solution of diphenylamine in H_2SO_4, the volume of the mixture was made up with water to 100-120 ml and the final solution titrated with 0.1 N $K_2Cr_2O_7$ until the solution acquired a violet-blue color.

Results for determination of tellurium by this method are given in Table 2.

The titrimetric method of determining tellurium is applicable to the determination of the latter in its alloys with antimony.

Tellurites are reduced by lactose in the presence of antimony also, as long as the latter is present in solution. However, on treating an antimony-tellurium alloy with nitric acid, the antimony is precipitated as metaantimonic acid, which adsorbs large amounts of tellurous acid. On treating the alloy with aqua regia or other acids, the antimony dissolves completely, but during subsequent neutralization and dilution, antimony is precipitated in the form of its basic salts. In order to keep antimony in solution, we treated the alloys with a mixture of nitric and tartaric acid. Small amounts of Fe, As, Sn, Pb, Cd, Bi, C, Se, Cu and other elements may be present in these alloys in addition to antimony and tellurium. Fe, As, Bi, and Sn compounds, like the compounds of antimony, are not reduced to the metal by lactose in weakly alkaline media; they are kept in solution by means of tartaric acid. Tin behaves differently, in that appreciable amounts of it may be precipitated at the same time as the tellurium. This complicates the analytical procedure considerably, since there is formed an amorphous, finely dispersed precipitate, consisting of tellurium and tin compounds. When the tin content is low, such complications are not observed. Lead and cadmium, when present in small amounts, do not interfere with tellurium determination. Carbon does not dissolve in nitric acid and can be removed by filtration. The elements which exhibit the greatest interference are copper and selenium which are precipitated together with tellurium during reduction by means of lactose. Thus, copper and selenium should be removed before proceeding with reduction of tellurium. This would complicate analysis appreciably.

We tried to solve this problem by establishing conditions whereby it would be possible to reduce tellurium in the presence of copper and selenium, rather than resorting to removal of copper and selenium beforehand. With this aim in view, tellurites were reduced by means of various reducing agents, which, in our opinion, should hold the copper and selenium strongly enough in the form of complexes. The best results were obtained when potassium ferrocyanide was used. In the presence of this compound, copper and selenium, in weakly alkaline media, are not only not reduced to the metals by such moderate reducing agents as lactose, but are not even reduced by stannite; at the same time, potassium ferrocyanide does not interfere with reduction of tellurium and does not affect the rate at which it separates out. The composition of the ferrocyanide complexes formed under these conditions are not considered in the present article. Investigations along these lines are being continued.

Tellurium was determined as follows.

An aliquot of alloy containing 0.0050-0.0300 g of tellurium was treated on heating with a mixture of nitric and tartaric acids. The composition of this mixture was: 3 volumes of HNO_3 sp.gr. 1.40 and 4 volumes of 30 % tartaric acid. 20 ml of this mixture was used for 1 g of alloy. Prolonged boiling should be avoided, as well as insufficient tartaric acid. Otherwise, antimony, in the form of meta-antimonic acid, may be precipitated under the conditions used for reduction of the tellurium. When the sample had dissolved, nitrogen oxides were removed by boiling the solution for a short period. It was found useful to add 5-10 ml of water during this process. When, after the alloy had dissolved, there remained black particles, these were filtered off and the filtrate obtained neutralized with 40 % NaOH using phenolphthalein as indicator, 6-8 drops of the alkali was added in excess, followed by 2-3 ml of 2 N $K_4Fe(CN)_6$, and 5 ml of a 20 % solution of lactose. The volume of the solution was then made up to 50-60 ml with water and the whole boiled for 5-10 minutes until the precipitate had coagulated completely, the latter being stirred periodically. The precipitate was filtered off on a plug of glass wool and asbestos, and washed with a 2 % solution of Na_2SO_4. The precipitate was dissolved, on heating, in a mixture of 20-25 ml of 0.1 N $K_2Cr_2O_7$ and 10 ml 4 N H_2SO_4. After the tellurium had dissolved completely, 15-20 ml of a 0.1 solution of Mohr's salt was added to the cooled mixture, followed by 5 ml of H_3PO_4 1 : 1, and 10-15 ml of 2 N HCl. The mixture was diluted to 100-120 ml with water and 3 drops of diphenylamine solution added; the excess Mohr's salt was finally titrated with 0.1 N potassium dichromate.

In order to give an idea of the reproducibility of the results we give below those obtained for two samples of antimony-tellurium alloys. Sample 1: Tellurium found in %: 2.93; 2.94; 2.97; 2.93; 2.96; 2.96. Amount found gravimetrically: 2.95 %. Sample 2: Tellurium found, in %: 9.51; 9.52; 9.55; 9.54; 9.57. Amount found gravimetrically: 9.55 %.

These results show that the method ensures good reproducibility. The deviation from the mean value for a tellurium content of about 3 % (sample 1) does not exceed 0.02 %, while for a tellurium content of about 10 % (sample 2) the deviation does not exceed 0.03 %.

SUMMARY

1. A rapid method has been developed for the quantitative reduction of tellurite to elemental tellurium in weakly alkaline media by means of lactose; the method permits rapid gravimetric and titrimetric determination of tellurium with a high degree of accuracy.

2. A titrimetric method has been developed for determining tellurium in antimony-tellurium alloys. Small amounts of As, Sn, Bi, Fe, Pb, Cd, Cu, and Se do not interfere.

Potassium ferrocyanide in weakly alkaline media prevents reduction of copper and selenium to the elemental state.

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ABSORPTION OF SULFUR OXIDES BY SILICATES

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Lead chromate, lead dioxide, or metallic silver have been used in elemental organic analysis for combining with the oxides of sulfur which are formed during the combustion of organic compounds. Lead dioxide has a number of disadvantages and is hardly used at all at present. Lead chromate readily corrodes the quartz tubes at high temperatures, and has a comparatively low melting point. Metallic silver which is an excellent absorbent not only for sulfur oxides, but also for the halogens [1] is, however, expensive and not very readily available, in addition, at temperatures of 700-900°, silver may corrode the quartz tubes.

We have already pointed out in one of our previous articles [2] that sodium and potassium silicates may be used instead of silver for trapping sulfur oxides. The present article is devoted to a study of the absorptive capacity of a number of other silicates.

Silicates to be used for quantitative analysis should be refractory, and should not absorb CO_2 and water vapor, further, they should rapidly and quantitatively absorb sulfur oxides and should not corrode quartz tubes; the sulfate formed as the result of absorption of the sulfur oxides should be stable at elevated temperatures (700-800°).

TABLE 1

Anion / Cation	Melting (or decomposition point, in deg C			Notes
	SO_4^{2-}	CO_3^{2-}	SiO_3^{2-}	
Na^+	884	851	1088	
K^+	1076	891	976	
Mg^{2+}	1124	350	—	
Ca^{2+}	1450	825	1540	
Sr^{2+}	1580	1497	1580	At 60 atm.
Ba^{2+}	1580	1740	1604	At 90° atm.
Zn^{2+}	740	300	1437	Decomposes
Cd^{2+}	1000	500	1242	Decomposes
Al^{3+}	770	—	1860	
Pb^{2+}	1000	315	766	

Table 1 contains some properties of a number of silicates. Tests showed that sodium and potassium silicates absorb atmospheric moisture and corrode the tubes. Lead silicate has a low melting point. Of the other silicates, according to our results, magnesium silicate exhibits the weakest absorptive capacity for sulfur oxides (Table 2).

It is interesting to note that the absorptive capacity of the silicates which we studied drops appreciably with decreasing temperature. Quantitative absorption of sulfur oxides by the silicates can be explained by two factors: 1) by the rapid absorption of sulfur trioxide; and 2) by the shift of the equilibrium toward formation of sulfur trioxide as the latter is absorbed by the silicate: $SO_3 + BaSiO_3 \rightleftharpoons BaSO_4 + SiO_2$; $2SO_2 + O_2 \rightleftharpoons 2SO_3$.

Sulfur oxides are absorbed fairly well by lead chromate, but their absorption by the latter is very much inferior to the absorption of these oxides by barium, calcium, strontium, and cadmium silicates.

At low temperatures (from 350 to 500°) nitrogen oxides are poorly absorbed. On increasing the temperature to 600-700°, complete dissociation of nitrogen dioxide to nitric oxide and oxygen occurs. The reverse reaction — formation of nitrogen dioxide — is comparatively slow at low temperatures, consequently silicates are not suitable for trapping nitrogen oxides.

During absorption of halogens, the silicates form chlorides, which, at high temperatures and in a strong stream of oxygen, can be carried through by the latter and thereby distort the analytical results.

Silicates are of great interest for analysis of sulfur-containing materials. We have established that, as a

TABLE 2

(Weight of Sulfosalicylic Acid 0.1 g)

Absorbent used for absorbing sulfur oxides	Length of silicate layer, in mm	Weight of silicate layer, in g	Temperature at which the silicate is heated, in deg C	O_2 throughput, in ml/ minute	Breakthrough of sulfur oxides	Observations
Magnesium silicate	100	14.7	600	250	Yes	At 100 mm layer of magnesium silicate was used for seven tests without breakthrough of sulfur oxides when the oxygen throughput was 250 ml/ minute
	200	29.4	600	250	"	
	100	14.7	700	250	No	
	100	14.7	700	250	"	
Cadmium silicate	100	11.6	700	120	"	
	100	11.6	700	120	"	
	100	11.6	700	120	"	
	100	11.6	700	200	"	
	100	11.6	700	250	"	
	100	11.6	700	330	Yes	
	200	23.2	700	330	No	
	200	23.2	700	600	"	
	200	23.2	700	650	Yes	
Manganese silicate	100	13.2	700	180	"	
	100	13.2	700	120	No	
	200	26.4	700	120	"	
	200	26.4	700	250	"	
	200	26.4	700	300	Yes	
Barium silicate	100	18.4	700	315	No	Breakthrough of sulfur oxides occurred during the 14 th test when the oxygen throughput was 150 ml/ minute, the length of the barium silicate layer was 50 mm
	100	18.4	700	315	"	
	50	9.2	700	315	"	
	50	9.2	700	315	Yes	
	50	9.2	700	315	"	
	50	9.2	700	200	"	
	50	9.2	700	150	No	
Calcium silicate	200	30.2	700	175	"	
	70	30.2	700	255	"	
	70	30.2	700	500	"	
	70	30.2	700	720	Yes	
	70	30.2	700	300	No	
	70	30.2	700	620	"	
	70	30.2	700	650	Yes	
	70	10.5	700	250	No	
	70	10.5	700	250	"	
	70	10.5	700	250	"	
	70	10.5	700	250	Yes	
	50	7.6	700	160	No	Breakthrough of sulfur oxides occurred in the seventh test when the oxygen throughput was 160 ml/ minute, and the length of the silicate layer was 50 mm
	50	7.6	700	160	"	
	50	7.6	700	160	"	
	50	7.6	700	160	No	
	50	7.6	700	160	"	
	50	7.6	700	160	"	
	50	7.6	700	160	"	

TABLE 2 (continued)

Absorbent used for absorbing sulfur oxides	Length of silicate layer, in mm	Weight of silicate layer, in g	Temperature at which the silicate is heated, in deg C	O_2 throughput, in ml/ minute	Break-through of sulfur oxides	Observations
Strontium silicate	200	31.00	700	480	No	Breakthrough of sulfur oxides was observed in the 24th test when the oxygen throughput was 160 ml/ minute and the length of the silicate layer was 50 mm
	200	31.00	700	650	"	
	100	15.50	700	110	"	
	100	15.50	700	375	"	
	100	15.50	700	390	"	
	50	7.75	700	130	"	
	50	7.75	700	160	"	
	50	7.75	700	320	"	
	50	7.75	700	400	"	
	50	7.75	700	430	Yes	
Lead chromate	100	–	600	200	No	On increasing the temperature, the chromate melted and the tube was spoiled
	200	–	600	280	"	
	200	–	600	340	"	
	200	–	600	500	"	
	200	–	600	555	"	
	200	–	600	610	Yes	

result of the rapid and efficient absorption of sulfur oxides by strontium, calcium, barium, and cadmium silicates, they can be used for the simultaneous determination of C, H, and S on one aliquot of test material. Two boats filled with silicate are placed at the forward edge of the tube for trapping the sulfur oxides. Because of the small surface area of the boats, the analysis cannot be carried out in a rapid oxygen stream. It is expedient to use large diameter tubes (see the experimental part).

EXPERIMENTAL

Commercial, filtered liquid glass (sodium silicate) can be used for preparing the silicates.

An approximately 10 % solution of sodium silicate and a solution of the appropriate salt (not the chloride) are gradually mixed with periodic stirring, until the insoluble silicate has finished depositing (test for complete precipitation). The bulky, friable precipitate is transferred to a beaker containing distilled water, the mixture is stirred and then allowed to stand for 30-40 minutes, and the silicate removed again by filtration. This treatment is repeated a few times until the filtrate gives no reaction for chloride ions. The final, filtered silicate is calcined for 5-6 hours at 700-800°.

The actual amount of insoluble silicates formed is usually much greater than one would expect on calculating on the basis of the metal silicate. Silicate precipitates corresponding in composition to the di- and trimetal silicate (or their mixtures) are prepared in this way. The silicates, with few exceptions (manganese silicate is brown) have a white color, have a low specific gravity and a large surface. Magnesium, calcium, strontium, and cadmium silicates exhibit negligible hygroscopicity. 10 g lots of these silicates do not change their weight by more than 0.02-0.03 g in the course of 10-15 days. At 700-800° they hardly corrode quartz tubes at all.

The absorptive capacity of the silicates was studied in the usual type of apparatus used for elemental analysis. Aliquots of sulfosalicylic acid (0.1-0.15 g) were subjected to combustion in a quartz tube 600-700 mm long (20 mm diameter) in an oxygen stream. The end of the tube was connected with a spiral potash bulb containing distilled water. Hardly any of the sulfur trioxide was held back by the potash bulb, and issued from the potash bulb as a white cloud. Even a negligible breakthrough of the sulfur oxides could be detected by the appearance of a small amount of a white smoke at the opening of the potash bulb.

The experimental results which are adduced in Table 2 show that the sulfur oxides are very efficiently absorbed by calcium, strontium, barium, and cadmium silicates.

Quantitative Trapping of Sulfur Oxides by Silicates. The results of these experiments enable us to develop a method for the quantitative determination of sulfur in organic materials by means of silicates.

TABLE 3

Test material and absorbent	Sample weight, in g	Increase in weight of the absorbent, in g	O_2 rate, in ml/ / minute	S found, in %	S calculated, in %	Difference between S found and S calculated in %	Observation
Sulfosalicylic acid	0.0996	0.0309	100	12.4	12.6	−0.20	The diameter of the tube was 20 mm, the silicates were ground to give a particle size of 1.5-2 mm and sieved free from dust, the silicate was loaded into two boats 70-80 mm long
(strontium silicate)	0.0843	0.0262	100	12.4	12.6	−0.18	
Sulfosalicylic acid	0.0486	0.0153	120	12.6	12.6	−0.02	
(calcium silicate)	0.0474	0.0146	120	12.3	12.6	−0.29	
Sulfosalicylic acid	0.0782	0.0246	95	12.5	12.6	−0.12	
(barium silicate)	0.0688	0.0216	95	12.6	12.6	−0.03	

For this purpose 2-3 boats 7-8 mm in length were placed inside the quartz tube. When sulfur-containing organic compounds were subjected to combustion in such a tube, the sulfur oxides formed, on passing over the heated (700-800°) boats, were completely absorbed by the silicates. Some of the results of this series of tests are given in Table 3. As a result of the small surface area of the boats, the oxygen throughput was kept down below 100 ml/minute, in order to avoid breakthrough of the sulfur oxides (for a tube diameter of 20-22 mm). When tubes fitted with ground glass joints and containing a longer layer of absorbent are used, the oxygen throughput can be increased considerably (to 200 and more ml/minute).

TABLE 4

Test material	Sample weight, in g	Increase in weight water, in g	Increase in weight, CO_2, in g	Found, in %		Calculated, in %		Difference, in %		Observations
				C	H	C	H	C	H	
Sulfosalicylic acid ($C_7H_6SO_6 + 2H_2O$)	0.0490	0.0182	0.0592	32.9	4.13	33.09	3.95	-0.15	+0.18	Calcium silicate 150 mm
	0.0504	0.0186	0.0612	33.1	4.10	33.09	3.95	+0.02	+0.15	Oxygen throughput 250 ml/ minute
Sulfonal ($C_7H_{16}S_2O_4$)	0.0544	0.0346	0.0734	36.8	7.06	36.82	7.05	-0.08	+0.01	Strontium silicate 150 mm
	0.0536	0.0350	0.0728	37.0	7.25	36.82	7.05	+0.21	+0.20	Oxygen throughput 250 ml/ minute
Dibenzylsufide ($C_{14}H_{14}S$)	0.0644	0.0388	0.1854	78.5	6.69	78.45	6.58	+0.06	+0.11	Strontium silicate 150 mm
	0.0536	0.0322	0.1542	78.5	6.67	78.45	6.58	+0.01	+0.09	Oxygen throughput 250 ml/ minute
Bis-(1,1-dimethyl-pentenesulfide)-3-($C_{14}H_{22}O_2S$)	0.0560	0.0446	0.1354	65.9	8.84	66.13	8.72	-0.19	+0.12	Strontium silicate 150 mm
	0.0462	0.370	0.1120	66.1	8.89	66.13	8.72	-0.03	+0.17	Oxygen throughput 250 ml/ minute

The results given in Table 4 show that it is possible to use silicates for absorbing sulfur oxides during determination of carbon and hydrogen in organic compounds containing sulfur. A silicate layer 15-20 cm long is used in the quartz tube instead of lead chromate in such analyses. Tests are being continued.

SUMMARY

During a study of the absorption of sulfur oxides by various silicates it was established that calcium, strontium, barium, and cadmium silicates absorb these oxides quantitatively at 700-800°. Strontium, barium, cadmium, and calcium silicates exhibit low hygroscopicity. The silicates studied do not corrode quartz tubes at 700-800°.

Calcium, strontium, barium, and cadmium silicates can be used for the simultaneous, quantitative determination of sulfur, carbon, and hydrogen in organic compounds.

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ANALYSIS OF HIGH MOLECULAR WEIGHT ORGANOSILICON COMPOUNDS BY INFRARED SPECTROSCOPY

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Chemical methods of analysis do not always allow one to determine the composition, and, in particular, the characteristic atomic groupings of a test compound. As the composition and the structure of the test compounds become more complex, the efficiency of chemical methods of analysis decreases more and more. By resorting to physicochemical and physical methods of analysis, e.g. by using spectrographic molecular analysis in the infrared, the problem can be solved very successfully.

TABLE 1

Atomic group	Frequency, in cm^{-1}	Wave length, in μ
Si—O	1050—1030	9.5—9.7
Si—Cl	810	12.3
	700	14.3
	467	21.4
	188	53.0
Si—I	355	28.1
Si—H	2210—2105	4.5—4.75
SiH_3	944—935	10.6—10.5
	921	10.85
	745—740	13.4—13.5
	713	14.0
	694—689	14.4—14.5
SiH_2	944—935	10.6—10.7
	892	11.2
	713	14.0
Si—D	1547	6.46
Si—C	1286—1162	7.8—8.6
$Si—CH_3$	1282	7.8
SiC_2H_5	1234—1219	8.1—8.2
SiC_3H_7	1190—1162	8.4—8.6
$Si(CH_3)_2$	832	12.0
$Si(CH_3)_3$	855	11.7
	832	12.0
	694—689	14.4—14.5
OH	3500—3330	2.86—3.20
Cyclic siloxanes		
Trimer	1020—1010	9.8—9.9
Tetramer	1090—1080	9.2—9.25

All the work carried out hitherto on the study of organosilicon compounds by infrared methods has been connected with the study of the infrared spectra of individual compounds, and the absorption maxima found in such work relate to certain chemical bonds and atomic groupings in the molecules of the test organosilicon compounds. No single solution has been found for certain problems (e.g. the question of the bands characterizing bonds [2, 3]). Nevertheless, even at this stage in the development of the field indicated, it has become possible to determine a number of atomic groups and bonds in the molecules of organosilicon compounds, for which characteristic absorption bands have been established.

In a previous article we turned our attention to the possibility of using infrared absorption spectroscopy for analyzing monomeric organosilicon compounds [4]. Table 1 has been compiled on the basis of our own studies and on published results [1-10].

We are unaware of any work devoted to infrared studies of high molecular weight compounds obtained by the interaction of various organosilicon compounds with organic or inorganic compounds. In the meantime, however, such compounds are finding wider application in the various fields of industry and in new techniques [11].

The article is devoted to the analysis of high molecular weight compounds obtained by the combination of organosilicon compounds with polymeric organic compounds which are characterized by the presence of free hydroxyl groups in their molecules.

TABLE 2

Test material	% SiO_2	% OH
Product of the initial condensation of glycerol with phthalic anhydride — A	—	7.8
Dimethyldichlorosilane — B	47	—
Product formed by interaction of A and B	10.8	0.4

TABLE 3

Test material	% SiO_2	% OH
Product of the initial condensation of glycerol with phthalic anhydride — A	—	7.8
Trimethylchlorosilane — B	55.5	—
Product formed by interaction of A and B	19.5	0.1

TABLE 4

Test material	% SiO_2	% OH
Product of the initial condensation of glycerol with phthalic anhydride — A	—	7.9
Ethyl ester of orthosilicic acid — B	28	—
Product formed by interaction of A and B	9.2	1.1

TABLE 5

Test material	% SiO_2	% OH
Product of the initial condensation of aniline and formaldehyde — A	—	4.8
Trimethylchlorosilane — B	55.5	—
Product formed by interaction of A and B	10.9	0.1

During a study of the materials obtained by the interaction of the initial condensation product of glycerol and phthalic anhydride, and also of the initial condensation product of aniline and formaldehyde with chlorinated silanes and tetraethoxysilane respectively, chemical analysis by Berley's method shows that there is a decrease in the number of hydroxyl groups in the final products, as compared with any of the original products containing OH-groups (Tables 2-7). Silicon can be determined (Tables 2-7) in the final products by a photocolorimetric method [12].

Using infrared absorption spectroscopy it was found possible to find a number of analytical features, by means of which the presence of certain atomic groups and chemical bonds can be established in the molecules of the organosilicon compounds, and which give an indication of the structure of the test materials and enable one to assess the changes which occur during the chemical transformations that take place.

The test materials used in the present investigation were obtained by combining the products of the initial condensation of glycerol and phthalic anhydride, and of the initial condensation of aniline and fomaldehyde, with trimethylchlorosilane, dimethyldichlorosilane, and tetraethoxysilane respectively.

TABLE 6

Test material	% SiO_2	% OH
Product of the initial condensation of aniline and formaldehyde — A	—	4.9
Dimethyldichlorosilane — B	47	—
Product formed by the interaction of A and B	6.4	0.3

TABLE 7

Test material	% SiO_2	% OH
Product of the initial condensation of aniline and formaldehyde — A	—	5.0
Tetraethoxysilane — B	28.8	—
Product formed by the interaction of A and B	9.4	0.9

These products were synthesized according to published methods [13,14]. The original and final products were subjected to careful purification, their purity being checked by their boiling point, specific gravity, refractive index, and infrared absorption spectra.

The infrared absorption spectra were photographed on an IKS-11 spectrophotometer. The source of illumination was a Nernst lamp which was fed by a stabilized electric current of 0.8 amperes at a voltage of 127 volts. The stability of the current applied to the lamp was ensured by means of a ferroresonance stabilizer and barreters. The infrared receiver was a vacuum-compensated radiation thermoelement with a manganin and constantan couple. A FEOU-15 photoelectrooptic amplifier was used for increasing the thermal currents; this amplifier is of the Kozyrev type. NaCl and LiF prisms were used as dispersion elements.

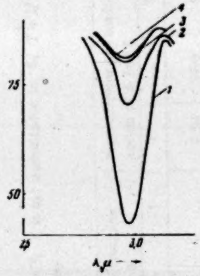

Fig. 1. Absorption maxima at 3 μ (3333 cm^{-1}) in the infrared absorption spectra of the product formed during the initial condensation of glycerol and phthalic anhydride — 1; and, in addition, of materials obtained by the interaction of this product with tetraethoxysilane — 2; with trimethylchlorosilane — 3; and with dimethyldichlorosilane — 4.

Measurements were carried out in the range 2.5 μ to 15 μ (6400-667 cm^{-1}). The absorption spectra of diphenylsilanediol, trimethylchlorosilane, and of the ethyl ester of orthosilicic acid were taken on 20% solutions of these materials in carbon tetrachloride, in the range 2-10 μ (5000-1000 cm^{-1}), and in carbon disulfide in the range 10 to 15 μ (1000-667 cm^{-1}).

The condensation product of glycerol with phthalic anhydride, and the products formed by reacting this condensation product with diphenylsilanediol, trimethylchloro-silane, dimethyldichlorosilane, and the ethyl ester of orthosilicic acid were studied in the form of films 18-20 μ thick. Film thickness was measured on a vertical IZV-1 cathetometer to an accuracy of 1 μ. The films were obtained by evaporating solutions of the test materials in acetone from plates of NaCl or KCl. In order to remove the last traces of solvent, the plates were finally dried in a vacuum desiccator.

The condensation product of aniline and formaldehyde, and also the materials formed by combining this product with trimethylchlorosilane, dimethyldichlorosilane, and tetraethoxysilane were studied in the form of tablets (d - 1.5 cm, weight 250 mg), obtained by pressing a mixture of KBr powder and the test material [15, 16]. Pressing was carried out in a special press-form, under a pressure of 7-8 ton / cm^2. 10 mg of the powdered test material was taken for 1 g of KBr.

A comparison was made of the spectra of the aniline-formaldehyde resin in the form of films, in the form in which it was precipitated from its solution in benzene, and in the form of tablets. The spectra proved to be identical, thus the methods are interchangeable.

On Fig. 1 are given the absorption bands at 3 μ (3333 cm^{-1}) for the initial condensation product of glycerol

TABLE 8

Wave length λ in μ; ν is the wave number in cm^{-1}; T is the transmission in %; $T = I/I_0 \times 100$, where I_0 is the intensity of the light stream before absorption, while I is the intensity after absorption

Product of the initial condensation of aniline and formaldehyde – A			Dimethyldichlorosilane $(CH_3)_2SiCl_2$ – B			Product formed by the interaction of A and B			Trimethylchlorosilane $(CH_3)_3SiCl$			Product formed by the interaction of A and C		
λ	ν	*T*		ν	*T*	λ	ν	*T*	λ	ν	*T*	λ	ν	*T*
2.94	3400	40	—	—	—	2.94	3400	40	—	—	—	2.94	3400	
2.98	3360	38	—	—	—	2.98	3360	37	—	—	—	2.98	3360	37
3.12	3200	57	—	—	—	3.12	3200	57	—	—	—	3.12	3200	57
3.33	3000	50	—	—	—	3.33	3000	50	—	—	—	3.33	3000	50
—	—	—	3.37	2960	39	3.37	2960	55	3.37	2960	34	3.37	2960	55
3.46	2890	49	3.49	2860	58	3.46	2890	49	3.49	2860	52	3.46	2890	49
3.53	2830	50	—	—	—	3.53	2830	50	—	—	—	3.53	2830	50
6.30	1585	15	—	—	—	6.30	1585	18	—	—	—	6.30	1585	20
6.74	1480	14	7.0	1430	60	6.80	1470	18		1440	55	6.74	1480	19
7.68	1300	21	—	—	—	7.68	1300	24	—	—	—	7.68	1300	26
7.98	1250	19	7.95	1260	35	8.00	1250	21	7.95	1260	15	8.00	1250	25
8.50	1175	31	—	—	—	8.50	1175	39	—	—	—	8.50	1175	47
8.90	1125	50	—	—	—	8.80	1140	48	—	—	—	8.90	1125	52
—	—	—	—	—	—	9.50	1050	50	—	—	—	9.60	1040	54
10.60	945	56	10.10	990	72	10.60	945	57	—	—	—	10.60	945	52
11.50	870	68	11.80	845	34	11.60	860	47	11.60	860	34	11.60	860	50
12.30	815	26	12.11	825	35	12.30	815	29	—	—	—	12.30	815	28
13.24	755	25	12.40	805	36	13.15	760	25	13.00	770	34	13.15	760	26
14.40	695	40	14.50	690	40	14.40	695	40	14.30	700	77	14.40	695	41

TABLE 9

Product of the initial condensation of glycerol and phthalic anhydride – A			Trimethylchlorosilane $(CH_3)_3SiCl$ – B			Product formed by the interaction of A and B			Dimethyldichlorosilane $(CH_3)_2SiCl_2$ – C			Product formed by the interaction of A and C		
λ	ν	T	λ	ν	T	λ	ν	T	λ	ν	T	λ	ν	T
2.98	3360	44	—	—	—	2.98	3360	82	—	—	—	2.98	3360	80
3.35	2980	28	3.37	2960	31	3.37	2960	26	3.37	2890	31	3.35	2980	28
3.50	2860	49	3.49	2860	52	3.50	2860	35	3.49	2860	52	3.50	2860	35
5.80	1725	28	—	..	—	5.80	1725	28	—	—	—	5.86	1715	35
6.20	1610	73	—	—	—	6.20	1610	67	—	—	—	6.20	1610	62
6.90	1450	62	6.94	1440	55	6.90	1450	48	7.07	1412	60	6.60	1515	49
7.95	1260	18	7.95	1260	15	7.95	1260	15	7.95	1260	35	8.00	1250	15
8.75	1140	29	—	—	—	8.75	1140	39	—	—	—	8.60	1160	37
9.00	1110	31	—	—	—	9.00	1110	38	—	—	—	9.00	1110	35
—	—	—	—	—	—	9.60	1040	57	—	—	—	9.60	1040	52
—	—	—	—	—	—	—	—	—	10.10	990	72	10.20	980	74
—	—	—	11.60	860	34	11.60	860	58	11.80	850	34	11.80	850	45
—	—	—	13.0	770	34	13.00	770	53	12.11	825	35	12.00	835	45
13.50	740	34	—	—	—	13.50	740	43	12.40	805	36	13.40	745	40
14.30	700	54	14.30	700	77	14.30	700	53	14.50	690	40	14.35	695	32

and phthalic anhydride — 1, and also for the materials obtained by the interaction of this product with tetraethoxysilane — 2; trimethylchlorosilane — 3; and dimethyldichlorosilane — 4. On Fig. 2 is shown the curve which shows the change in intensity of the absorption band at 3 μ (3333 cm^{-1}) in the spectrum of the product of initial condensation as trimethylchlorosilane is added to it.

These results lead one to conclude that the absorption band at 3 μ (3333 cm^{-1}) can be used as an analytical characteristic of the presence of an OH-group in similar high molecular weight compounds.

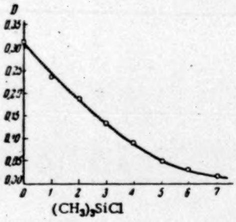

Fig. 2. Change in intensity of the absorption band at 3 μ (3333 cm^{-1}) in the infrared spectrum of the product formed by condensation of glycerol and phthalic anhydride as trimethylchlorosilane is added to it.

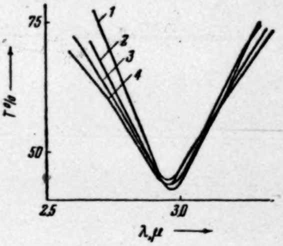

Fig. 3. Absorption maxima at 2.98 μ (3360 cm^{-1}) in the infrared absorption spectra of the product formed by the initial condensation of aniline and formaldehyde — 1; and also of the material formed by interaction of this initial condensation product with tetraethoxysilane — 2; trimethylchlorosilane — 3; and with dimethyldichlorosilane — 4.

On Fig. 3 are given the absorption bands at 2.98 μ (3360 cm^{-1}) for the initial product of the condensation of aniline and formaldehyde — 1; and also for the material obtained by the interaction of this product with tetraethoxysilane — 2; with trimethylchlorosilane — 3; and with dimethyldichlorosilane — 4. It is evident from Fig. 3 that the intensity of the absorption band hardly changes at all, although chemical analysis (Tables 5-7) indicated a significant decrease in OH-groups in the final products of the interaction as compared with the reactants. This is probably the consequence of the fact that the absorption bands of N—H and O—H bonds overlap and mask each other. We were unable to resolve these bands. Consequently, in high molecular weight compounds, similar to those we have studied, which contain N—H bonds, the use of the absorption band at 2.98 μ (3360 cm^{-1}) for analysis of OH-groups by infrared spectroscopy is considerably complicated at the present level of experimental technique.

It is clear from Tables 8 and 9 that in all cases where the initial organosilicon compound used as test material is an alkychlorosilane, a new absorption band appears in the spectrum of the final interaction product at 9.5-9.6 μ (1050-1040 cm^{-1}), which is not present in the spectrum of the original products. The appearance of this band can only be explained by the formation of a new atomic group Si—O as the result of a chemical process [3-5]:

$$R_xOH + ClSi(CH_3)_3 \xrightarrow{-HCl} R_x - OSi(CH_3)_3,$$

where R_x is a complex organic radical.

The formation of the atomic group Si—O always leads to the appearance of an absorption band at 9.5-9.6 μ (1050-1040 cm^{-1}). Accordingly, the band at 9.5-9.6 μ (1050-1040 cm^{-1}) may be used as an anlytical characteristic for establishing the presence of Si—O bonds in complex organosilicon compounds.

SUMMARY

1. An analytical method, based on the use of infrared absorption spectroscopy, has been developed for the analysis of polymeric organosilicon compounds obtained by interacting the products of the initial condensation

of glycerol and phthalic anhydride, and also of aniline and formaldehyde, with tetraethoxysilane, trimethylchlorosilane, and dimethyldichlorosilane.

2. It has been established that the absorption band at 9.5 - 9.6 μ (1050-1040 cm^{-1}) can be used as an analytical characteristic for the Si—O bond in similar high molecular weight compounds.

3. The absorption band at 3.00 μ (3333 cm^{-1}) can be used as a reliable criterion for the qualitative and quantitative determination of OH-groups in organosilicon compounds which do not contain N—H bonds, the absorption of the latter band at 3.00 μ (3333 cm^{-1}) overlaps the band characteristic of the O—H bonds.

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BROMOMETRIC METHODS FOR THE DETERMINATION OF UNSATURATED HYDROCARBONS IN ISOPENTANE-ISOPRENE-ISOAMYLENE MIXTURES

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During the catalytic dehydrogenation of isopentane there is formed a catalyzate which mainly consists of five components — the original isopentane, three isoamylenes, and isoprene; the ratio of the components of the mixture depend on the reaction conditions. The rather few published results [1, 2] on studies of such mixtures show that there is as yet no definite analytical method for such mixtures. One of the fundamental characteristics of hydrocarbon mixtures containing olefines, is the percentage total unsaturatedness of the mixtures expressed in bromine or iodine numbers, but even this simple determination is used in several variants. The most widely used methods of determining olefines in solution are the bromometric methods of Rosenmund [3], Kaufman-Gal'pern [4, 5], and Mcilliney-Virabiants [6, 7]. In contrast to the first two methods, the latter method makes an attempt to take into account the substitution reactions which occur during the bromination process. The Gal'pern and Rosenmund methods differ in the experimental conditions, and these differences lead to appreciable deviations during the determination of unsaturatedness of olefine mixtures. The reactions are not limited to combination of bromine molecules across the double bonds, but, depending on the conditions used, may be accompanied by a number of secondary processes [5, 8 - 10]. The ease with which one or another of these secondary reactions may occur depends primarily on the structure of the given olefine, as well as on bromination conditions — nature of the solvent, extent of dilution, temperature, etc. Petrov [8] who used the Kaufman method for studying the bromination of 120 various olefines in methanol solution, showed that the result of this reaction is determined by the structure of the hydrocarbons, and that some of them, for example, hydrocarbons with double bonds linking secondary and tertiary carbon atoms, combine with more than one equivalent of bromine. The difference between the calculated and experimental results is so great, that on the basis of these observations, the author suggested a method for evaluating the branching of the unsaturated hydrocarbons on the basis of their reactivity in bromination reactions. It is obvious that standard conditions which are suitable for the quantitative bromination of mixtures of any olefines, simply do not exist, accordingly, in principle, it is impossible to carry out an accurate determination of mixtures of olefines by any bromometric method. The conditions under which one of the olefines combines with exactly one molecule of bromine will prove unsuitable for others, in which, under the same conditions, there will occur clearly expressed secondary reactions or combination of bromine molecules will take place too slowly. In the first instance the analytical result will be high, while in the second it will be too low. It is also natural that solvents with different polarities will exhibit different activating effects on substitution reactions, and accordingly small deviations in the results obtained by analysis carried out according to different procedures will be unavoidable.

When the test mixtures contain diene hydrocarbons with conjugated double bonds, they will usually combine rapidly with one molecule of bromine, but react very much more slowly with a second bromine molecule [11, 12]. The percentage unsaturatedness of diene hydrocarbons is usually only slightly in excess of 50% when calculations are based on the assumption of the presence of two double bonds. The rate with which the bromine molecule combines with the hydrocarbon depends on the temperature of the medium and the duration of the reaction.

Thus, there is no single bromometric method which is capable of giving absolutely correct analytical results. Such methods as do exist can only be used with a fair degree of accuracy for the determination of the unsaturatedness of mixtures of olefine and diolefine hydrocarbons.

The present article is devoted to a comparative evaluation of the accuracy of bromometric methods of determining unsaturatedness, and to the choice of the most suitable method for the analysis of catalyzates obtained during dehydrogenation of isopentane. Three bromometric methods — those of Rosenmund, Gal'pern, and Virabiants — were checked on pure C_5 hydrocarbons, and also on mixtures of isopentane with isoamylenes and isoprene, differing in the number and concentration of the various components. It has been shown that the Virabiants method is not suitable for the analysis of such mixtures, since the experimental error is not constant, and amounts to 7-8 % absolute.

Results of the analyses carried out according to the Rosenmund and Gal'pern method confirmed that the accuracy of the determination of unsaturatedness depends on the structure of the hydrocarbons (or the composition of the mixture). 2-Methylbutene-2 and 3-methylbutene-1 brominate without complications and combine with one molecule of bromine, while 2-methylbutene-1 absorbs more than one molecule of bromine. Bromination of isoprene by the Rosenmund and Gal'pern methods also leads to high results (assuming one double bond).

Analysis of two component mixtures of isopentane with the isomeric isoamylenes shows that both methods could be used for studying such mixtures, the accuracy achieved being ± 1 % absolute. An exception is the mixture of isopentane with 2-methylbutene-1, analysis of which by the Rosenmund method gives results which are too high by 13 %; this corresponds to the extent by which the results obtained during determination of the unsaturatedness of pure 2-methylbutene-1 are too high (see below in mixtures 15-17). Results on the analysis of three and four component mixtures indicate that as long as such mixtures do not contain isoprene (see below, mixtures 18-23, 38-40, 28-29), the absolute experimental error for determination of the olefines is on the average equal to ±1 %; on adding isoprene to three component mixtures, the analytical error increases to ± 3 % absolute.

From the analytical results for five-component isopentane-isoprene-isoamylenes mixtures, it follows that for isoprene contents in these mixtures of up to 20 %, the experimental error is on an average + 3% absolute by the Rosenmund method, and −2 % absolute by the Gal'pern method (see below in mixtures 30-36 and 42-44).

Since the catalyzates obtained during dehydrogentation of isopentane are also five-component mixtures with a low isoprene content, we tried to use the results obtained on similar synthetic mixtures in order to establish the unsaturatedness of the catalyzates.

Since the mean error in the determination of unsaturatedness in five-component mixtures is systematic in character in both methods, it should be possible to apply corrections to the final results (for isoprene contents of the mixtures of up to 20 %). Experiment confirmed the correctness of this assumption. Comparison of the total unsaturated hydrocarbons in seven catalyzates obtained from the dehydrogenation of isopentane, as determined by the two methods, shows that on introducing correction factors, the values obtained for unsaturated hydrocarbons in the catalyzates, by the Rosenmund and Gal'pern methods, practically coincide.

Bromination methods only enable total determination of ethylene and diene hydrocarbons to be carried out; determination of olefines in the presence of dienes is, in principle, impossible, and the true content of the mono-olefines can only be found by the difference between total unsaturated hydrocarbons and the content of diene hydrocarbons. For correct evaluation of the amount of isoamylenes in the catalyzates, which may contain isoprene, it is necessary to make corrections to the bromometric results.

Isoprene can be determined quantitatively by means of general methods which are applicable for the determination of diene hydrocarbons. These methods differ from each other in principle, and each of them is based on some reaction which is characteristic of diene compounds. Such methods include the diene condensation with maleic or chloromaleic anhydride [13, 14], the catalytic hydrogenation of dienes by the Dolgoplosk method [15], the volumetric diazometric method of coupling dienes with diazotized p-nitroaniline [16], and the Robey - Wiese photometric method [17].

The common drawback of all the methods indicated is the long time to carry them out. One determination takes up to 8 hours, and even the most rapid method — the photometric one — takes about 1.5 hours. The accuracy of diene determination varies from 0.3-3 % absolute, depending on the technique employed.

The Robey - Wiese is not a general method for analysis of dienes, but relates specifically to determination of isoprene; it is based on the coloration of strongly diluted solutions of isoprene in absolute methanol on heating the solution with mercuric acetate. The appearance and the intensity of the color is independent of the presence in the test material not only of mono-olefines, but also of other dienes — piperylene and cyclopentadiene. The technique which these authors have developed is suitable for the analysis of mixtures containing up to 50 % of isoprene (in the presence of a large amount of piperylene); further increases in the concentration of the isoprene necessitate greater dilution of the solutions. The experimental error, according to the authors, is ± 1 %; one determination takes about 1.5 hours.

We used the Robey - Wiese method in the present work for studying isopentane-isoprene-isoamylene mixtures. A preliminary check on the method, using synthetic three-, four-, and five-component mixtures of isoprene with isopentane, 2-methylbutene-2, 2-methylbutene-1, and 3-methylbutene-1, demonstrated that this method is fully applicable for such determinations.

In all cases good agreement was obtained between the experimental and calculated isoprene concentrations. The mean experimental error was less than 1% absolute, and one determination took 1 hour 20 minutes; when series of determinations were carried out, the time for one analysis was cut down to 20 minutes. The photometric method of studying mixtures containing isoprene is convenient in view of the simplicity of the technique, since it does not require numerous accurate weighings or titrations. This advantage, together with its satisfactory accuracy and rapidity, permits one to recommend this photocolorimetric method as a control method for the determination of isoprene under production conditions.

Thus, knowing the isoprene concentration of isopentane-isoprene-isoamylene mixtures, the true content of the isoamylenes (P) can be calculated by means of the formula:

$$P = \alpha P' - b, \qquad (1)$$

where P' is the total amount of unsaturated hydrocarbons found in the mixture; b is the isoprene concentration of the mixture; while α is the correction factor (for the Rosenmund method $\alpha = 0.96$, while for the Gal'pern method $\alpha = 1.04$).

Just at the time when the present work was being finished and was being prepared for publication, a short communication by Timofeeva et al.[8] appeared; this dealt with the analysis of mixtures of isopentane with the isoamylenes and isoprene by a bromometric method.

In contrast to our conclusions, the correction factor which Timofeeva et al. introduced into the final formula they used, only took into account errors introduced as the result of inexact bromination of isoprene.

In order to prepare the synthetic mixtures used in our work, the following hydrocarbons were prepared and isolated in a pure state:

Isopentane. The commercial product after purification by distillation through a column with an efficiency of 30 theoretical plates had a boiling point of 27.9° (760 mm); n_D^{20} 1,3537; d_4^{20} 0.6194.

The Isoamylenes were prepared by dehydration of isoamyl alcohol over activated alumina at 350 and 500° at a volume rate of 0.5-1 liter/hour. The fraction of catalyzate boiling up to 40° was boiled with sodium metal, after which it was fractionally distilled in a laboratory column with a copper packing, the efficiency of which was about 100 theoretical plates. The three isoamylenes were separated:

2-methylbutene-2 (b.pt. 38.6 (760 mm), n_D^{20} 1.3874, d_4^{20} (0.6622);

2-methylbutene-1 (b.pt. 31.0 (760 mm), n_D^{20} 1.3778, d_4^{20} (0.6502);

3-methylbutene-1 (b.pt. 20.0 (760 mm), n_D^{20} 1.3641, d_4^{20} (0.6270).

Isoprene. The commercial product was purified from impurities through its cyclic adduct with SO_2 [19]; after distillation through a column with a plate efficiency of 35, it had a boiling point of 34.1° (760 mm), n_D^{20} 1.4218; d_4^{20} 0.6805.

Synthetic mixtures were prepared from the individual components weighed out on an analytical balance. The total content of unsaturated hydrocarbons was determined by three methods:

Rosenmund's Method [3]. The bromine solution (0.1 N) was prepared in glacial acetic acid to which pyridine and sulfuric acid were added. The bromine solution was standardized against thiosulfate. The test aliquot was dissolved in chloroform.

Gal'pern's Method. [5]. The bromine solution (0.2 N) was prepared in methanol saturated with sodium bromide. The methanol was distilled, without preliminary standing over potassium hydroxide, through a column with a glass packing and with an efficiency of 30 theoretical plates. Test aliquots were dissolved in methanol.

Virabiants' Method [6]. The bromine solution (0.2 N) was prepared in carbon tetrachloride. The test aliquots were also dissolved in carbon tetrachloride.

Experimental Procedure. 10 ml of solvent, and the sample sealed up in a thin walled glass ampoule, were introduced into a 200 ml Erlenmeyer flask with a ground glass stopper. Both the ampoule and the solvent were cooled beforehand. The ampoule was broken by means of a glass rod and the bromine solution added to the flask until the appearance of a stable yellow color. The subsequent procedures followed, depending on the method chosen for determining the amount of unsaturated hydrocarbons. The aliquots of the samples taken were weighed out on an analytical balance. The sample weights ranged from 0.15-0.2 g in the case of the Rosenmund method, up to 0.1 g in the case of the Gal'pern method, and up to 0.15 g for the Virabiants method.

TABLE 1

Percentage of Unsaturated Hydrocarbons in Isoamylenes and Isoprene in Weight %

Hydrocarbon	Rosenmund method		Gal'pern method		Virabiants' method	
	Found	Error, absolute, in %	Found	Error, absolute, in %	Found	Error, absolute, in %
2-Methylbutene-2	99.8	-0.2	98.9	-1.1	95.0	-5.0
3-Methylbutene-1	99.8	-0.2	98.8	-1.2	96.6	-3.4
2-Methylbutene-1	112.4	+12.4	103.2	+3.2	92.2	-7.8
Isoprene*	106.5	+6.5	104.6	+4.6	100.3	+0.3

* Calculations for unsaturatedness are based on one double bond.

Results for the determination of the percentage unsaturated hydrocarbons in the isoamylenes and in isoprene are given in Table 1, while the unsaturated hydrocarbon contents of synthetic mixtures are given in Tables 2 and 3. The values quoted in the tables wich indicate the unsaturated hydrocarbon content in weight percent, are the means of several determinations.

The correction factor α, in the case of determination of unsaturated hydrocarbon content by the Rosenmund or Gal'pern methods, was calculated as the mean deviation of the caluclated content of unsaturated hydrocarbon in mixtures from the value determined experimentally (mixture 35 was not taken into account).

Table 4 contains the means results obtained for determination of unsaturated hydrocarbons in catalyzates from catalytic dehydrogenation of isopentane, carried out under various conditions. The values for the unsaturated hydrocarbon content of catalyzates as determined by the Rosenmund method are higher than those obtained by the Gal'pern method, as in the case of five-component synthetic mixtures. On introducing the necessary correction factor α, the values for the unsaturated hydrocarbon content of the catalyzates as determined by the Rosenmund and Gal'pern methods become very similar to each other, and the mean deviation between the two methods amounts to 0.5 % absolute.

Determination of isoprene in isopentane-isoprene-isoamylene mixtures was carried out on the FEK-M photoelectric colorimeter using a blue filter. The calibration curve was constructed with the aid of standard solutions of chemically pure isoprene in absolute methanol.

Analytical Procedure for Isoprene. 95-97 ml of absolute methanol was introduced into a 100 ml standard flask, which was then stoppered and weighed on an analytical balance. 1 ml of test mixture was then introduced into the flask by means of a pipet whose tip was placed just in the alcohol surface, the flask was then weighed again, and the volume of the solution made up to the mark with methanol. The solution was carefully mixed and kept in a cold place away from light. 2.5 g of mercuric acetate was weighed out into each of two test tubes of 15-20 ml, exactly 1 ml of the solution prepared and 10 ml of methanol were added, and the tubes sealed while

TABLE 2

Two-, Three-, and Four-Component Mixtures

Number of mixture	Composition of mixtures in % weight						Unsaturated hydrocarbon content of mixture in % weight					
	Iso-pentane	2-Methyl-butene-2	2-Methyl-butene-1	3-Methyl-butene-1	Iso-prene•	Calcul. unsat. hy•drocarbon content	Rosenmund method		Gal'pern method		Virabiants method	
							Found	Error absol. in %	Found	Error absol. in %	Found	Error absolute in %
1	49.8	50.2	—	—	—	50.2	50.4	+0.2	49.4	−0.8	47.8	−2.4
2	57.3	42.7	—	—	—	42.7	43.1	+0.4	42.5	−0.2	40.5	−2.2
3	38.4	61.6	—	—	—	61.6	61.2	−0.4	60.4	−0.2	60.5	−1.1
5	62.6	37.4	—	—	—	37.4	38.3	+0.9	36.6	−0.8	34.4	−3.0
12	93.7	—	—	6.3	—	6.3	6.5	+0.2	5.2	−1.1	4.4	−1.9
13	85.2	—	—	14.8	—	14.8	15.5	+0.7	15.7	+0.9	12.6	−2.2
14	50.1	—	—	49.9	—	49.9	49.8	−0.1	51.1	+1.2	46.9	−3.0
15	95.3	—	4.7	—	—	4.7	5.3	+0.6	3.8	−0.9	3.0	−1.7
16	85.7	—	14.3	—	—	14.3	16.5	+2.2	12.6	−1.7	12.1	−2.2
17	51.3	—	48.7	—	—	48.7	54.3	+5.6	47.9	−0.8	42.3	−6.4
18	71.8	18.8	9.4	—	—	28.2	28.7	+0.5	29.5	+1.3	23.3	−4.9
19	56.3	19.2	24.5	—	—	43.7	46.2	+2.5	43.9	+0.2	39.5	−4.2
20	61.2	29.3	9.5	—	—	38.8	38.8	0.0	38.6	−0.2	34.5	−4.3
21	77.1	18.5	—	4.4	—	22.9	22.7	−0.2	22.5	−0.4	20.2	−2.7
22	69.1	21.7	—	9.2	—	30.9	30.7	−0.2	30.1	−0.8	26.1	−4.8
23	66.0	30.1	—	3.9	—	34.0	33.7	−0.3	32.8	−1.2	30.6	−3.4
38	79.6	—	9.9	10.5	—	20.4	19.1	−1.3	20.7	+0.3	16.9	−3.5
39	69.8	—	9.8	20.4	—	30.2	28.1	−2.1	31.1	+0.9	26.0	−4.2
40	69.0	—	21.1	9.9	—	31.0	30.6	−0.4	32.1	+1.1	26.9	−4.1
9	45.1	54.4	—	—	0,5	54.9	55.4	+0.5	55.4	+0.5	52.7	−2.2
6	56.1	41.0	—	—	2,9	43.9	45.6	+1.7	42.9	−1.0	39.9	−4.0
7	34.5	62.7	—	—	2,8	65.5	67.6	+2.1	63.0	−2.5	64.7	+0.8
10	42.9	53.6	—	—	3,5	57.1	56.0	−1.1	59.7	+2.6	51.4	−5.7
8	39.4	55.0	—	—	5,6	60.6	61.8	+1.2	59.6	−1.0	60.9	+0.3
11	35.9	54.9	—	—	9,2	64.1	66.1	+2.0	66.3	+2.2	60.9	+3.2
4	49.6	33.4	—	—	17,0	50.4	53.6	+3.2	50.6	+0.2	48.2	−2.2
24	87.5	—	—	9.3	3,2	12.5	13.2	+0.7	13.4	+0.9	9.8	−2.7
25	80.2	—	—	9.3	10,5	19.8	21.7	+1.9	20.2	+0.4	18.0	−1.8
26	87.5	—	9.8	—	2.7	12.5	14.2	+1.7	12.9	+0.4	11.1	−1.1
27	80.1	—	9.9	—	10,0	19.9	22.0	+2.1	19.9	±0.0	17.6	+2.3
28	64.1	20.3	10.6	5.0	—	35.9	37.3	+1.4	34.4	−1.5	32.3	−3.3
29	51.9	19.4	23.4	5.3	—	48.1	49.5	+1.4	47.4	−0.7	44.1	−4.0

• Calculations for unsaturated hydrocarbon content are based on the assumption of the presence of one double bond.

TABLE 3

Five-Component Mixtures

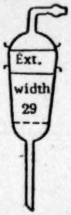
Number of mixture	Composition of mixtures in % weight						Unsaturated hydrocarbon content of mixture in % weight					
	Iso-pentane	2-Methyl-butene-2	2-Methyl-butene-1	3-Methyl-butene-1	Iso-prene•	Calc. un-satur. hy•drocarbon content	Rosenmund method		Gal'pern method		Virabiants method	
							Found	Error absol. in %	Found	Error absol. in %	Found	Error absol. in %
30	55.3	24.2	10.0	5.0	5.5	44.7	46.6	+1.9	43.1	−1.6	41.9	−2.8
31	45.7	25.3	19.8	4.6	4.6	54.3	56.2	+1.9	51.6	−2.7	51.3	−3.0
32	59.3	25.0	10.0	5.0	0.7	40.7	43.1	+2.4	39.8	−0.9	37.4	−3.3
33	56.4	26.0	9.7	4.8	3.1	43.6	44.9	+1.3	41.0	−2.6	37.5	−7.1
34	49.1	25.8	10.2	4.6	10.3	50.9	53.7	+2.8	48.2	−2.7	47.2	−3.7
35	39.5	25.6	10.1	4.6	20.2	60.5	65.8	+5.3	57.6	−2.9	60.3	−0.2
36	44.3	25.6	10.0	15.0	5.1	55.7	58.3	+2.5	53.8	−1.9	49.8	−5.9
42	33.5	28.2	11.0	5.2	22.1	66.5	69.8	+3.3	64.5	−2.0	62.6	−3.9
43	47.2	25.6	9.7	4.6	12.9	52.8	56.0	+3.3	51.1	−1.7	49.2	−3.6
44	43.6	25.4	9.8	4.4	16.8	56.4	58.8	+2.4	54.8	−1.6	53.6	−2.8

• Calculations for unsaturated hydrocarbon content are based on the assumption of the presence of one double bond.

TABLE 4

Determination of the Unsaturated Hydrocarbon Content of Catalyzates in Weight %

No. of the catalyzate	Without application of cor. factor α			After application of correction factor α		
	Rosenmund method	Gal'pern method	Deviation abs. in %	Rosenmund method	Gal'pern method	Deviation abs. in %
1	57.1	52.5	4.6	54.8	54.6	0.2
2	37.5	35.3	2.2	36.0	36.7	0.7
3	47.8	43.3	4.5	45.9	45.0	0.9
4	34.4	32.2	2.2	33.0	33.5	0.5
5	50.1	45.2	4.9	48.1	47.0	1.1
6	59.2	54.6	4.6	56.8	56.8	0.0
7	27.7	25.5	2.2	26.6	26.5	0.1



being cooled. The fused tubes were immersed in a water bath operating at 60 ± 1°, the mercuric acetate dissolved on rapid agitation of the tubes; the tubes were then kept at 60° for exactly one hour. When the hour had elapsed, the tubes were cooled under the tap for 5-7 minutes and unsealed, the contents were filtered rapidly under dry air pressure through a porous No. 3 glass filter (see diagram). The optical density of the filtrate was determined immediately; two parallel determinations may differ by 0.002-0.003 units. The glass filters and cells were washed after use with concentrated hydrochloric acid and water, and rinsed with distilled water, alcohol, and dry acetone, in turn.

TABLE 5

Determination of Isoprene and Calculation of the Concentrations of Isoamylenes in Synthetic Mixtures

Number of the mixture	Composition of the mixture in % weight				Isoprene		Calculation of the concentration of the isoamylenes in the mixtures by means of formula (1)					
							Methods for determ. unsat hydrocarbon content (%wt.)		Concentrations of isoamylenes			
									Rosenmund method		Gal'pern method	
	Isopentane	Total content of isoamylenes	Isoprene*	Calc. unsaturated hydrocarbon content of the mixture	Found, in % weight	Error, absolute, in %	Rosenmund	Gal'pern	Found	Error, absol. in %	Found	Error absolute in %
9	45.1	54.4	0.5	54.9	0.7	+0.2	—	—	—	—	—	—
10	42.9	53.6	3.5	57.1	4.0	+0.5	—	—	—	—	—	—
11	35.9	54.9	9.2	64.1	8.8	—0.4	—	—	—	—	—	—
28	64.1	35.9	—	35.9	0.2	+0.2	—	—	—	—	—	—
31	47.7	49.7	4.6	54.3	4.6	0.0	54.0	53.7	49.4	—0.3	49.1	—0.6
32	59.3	40.0	0.7	40.7	1.2	+0.5	41.4	41.4	40.2	+0.2	40.2	+0.2
33	56.4	40.5	3.1	43.6	3.7	+0.6	43.1	42.6	39.4	—1.1	38.9	—1.6
34	49.1	40.6	10.3	50.9	10.3	0.0	51.5	50.1	41.2	+0.6	39.8	—0.8
35	39.5	40.3	20.2	60.5	20.9	+0.7	63.2	59.9	42.3	+2.0	39.0	—1.3
36	44.3	50.6	5.1	55.7	5.6	+0.5	56.0	56.0	50.4	—0.2	50.4	—0.2
42	33.5	44.4	22.1	66.5	21.8	—0.3	67.0	67.0	45.2	+0.8	45.2	+0.8
43	47.2	39.9	12.9	52.8	12.0	—0.9	53.7	53.1	41.7	+0.8	41.1	+0.2
44	43.6	39.6	16.8	56.4	17.2	+0.4	56.4	56.9	39.2	—0.4	39.7	+0.1

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* Calculations of the unsaturated hydrocarbon content are based on the assumption of the presence of one double bond.

The percentage by volume of isoprene in the test sample was determined with the aid of a calibration curve, the percentage by weight being found by calculation according to the formula: $b = \frac{c.d}{0.6805}$, where c is the content of isoprene in percentage volume as found, while d is the weight of the aliquot of the hydrocarbon mixture taken in g.

Results of analyses of synthetic mixtures with various ratios of the components are given in Table 5.

SUMMARY

1. A check has been carried out on three analytical methods (Rosenmund, Gal'pern, and Virabiants) for the determination of the total amount of unsaturated hydrocarbons in synthetic mixtures of isopentane-isoprene- and the isoamylenes.

2. It has been shown that under the conditions used in these methods, one molecule of 2-methylbutene-1 and of isoprene combined with more than one molecule of bromine.

3. It has been established that, depending on the qualitative and quantitative composition of the mixtures tested, the accuracy of determination of total unsaturated hydrocarbons by the Rosenmund and Gal'pern method, varies from ± 1 to ± 3 % absolute.

4. Correction factors are suggested which permit determinations to be carried out with an accuracy of ±1 % absolute, for both the total percentage of unsaturated hydrocarbons and for the total content of isoamylenes in mixtures of isopentane with the three isoamylenes and isoprene.

5. It has been shown that the Virabiants method is not suitable for the analysis of the mixtures indicated.

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A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF REDUCING SUGARS IN WOOD HYDROLYZATES AND SULFITE LIQUORS BY PAPER CHROMATOGRAPHY

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During the investigation of the composition of wood hydrolyzates and sulfite liquors, their sugar content is estimated on the basis of the total reducing materials present. This determination always gives high results, since the reducing materials present in the wood hydrolyzates and sulfite liquors are a mixture of reducing sugars (glucose, mannose, galactose, fructose, xylose, arabinose, rhamnose, etc.) and reducing materials which are not sugars (furfural, uronic acid, etc.). In order to improve the technology of the production of alcohol and nutrient yeast in fermentation and sulfite-alcohol factories, it is essential to be in a position to determine each sugar separately in the production liquors, at the various stages of the technological process.

Most of the methods published for the separation of sugars by one-dimensional paper chromatography permit separation of mixtures of sugars consisting of only 3-4 components, accordingly, they are not applicable to the analysis of wood hydrolyzates and sulfite liquors, in which it is necessary to separate 7-10 materials with similar R_f values.

For separating sugars in wood hydrolyzates [1] and sulfite liquors [2] by means of one- and two-dimensional paper chromatography, some research workers take 16 days.

It has been suggested that the amounts of the various sugars on the chromatogram be determined either by methods based on measurement of the area and intensity of the colored spots after development [3, 4], or by various micro methods after extraction of the sugars from the chromatogram [5-9].

The use of such methods often requires expensive reagents and apparatus; they frequently do not yield results of sufficient accuracy, and take a lot of time.

We have developed a method for the separation of sugars in wood hydrolyzates and sulfite liquors on a one-dimensional paper chromatogram, and also a method for the quantitative determination of the sugar extracted from the chromatogram. Separation of all the sugars in the hydrolyzates takes 2-3 days. Determination of the sugar extracted from the chromatogram, within the limits of 10 to 2500μg, can be carried out in 10 minutes with an accuracy of ± 2 %.

Experimental Procedure

Separation of the sugars is realized on a descending chromatogram, with continuous removal of the solvent passing through the paper (Fig. 1). Contact between the bottom end of the chromatogram and the neck of a small flask (serving as a receiver) creates the conditions for the continuous, uniform movement of the solvent during the time the chromatogram is allowed to run, which is essential for separation of the materials.

The solvent used is the upper layer obtained from a mixture of ethyl acetate, pyridine, and water (5 : 1 : 5). Chromatograms are run simultaneously on 12-14 paper strips 3 x 45 cm under a glass cover. Aliquots of the test hydrolyzate or sulfite liquor are placed on 10 (or 12) of these strips. On the 11th or 13th strip a sample of the same test solution to which glucose has been added is placed, while on the 12 th strip (or 14 th strip), some more of the same test solution to which xylose has been added is applied. These last strips act as indicators.

Exact measurement and application of test solution is carried out by means of the micro-pipet shown on Fig. 2. The top end of the pipet is connected to a rubber bulb, which is fitted into a metal case. A micro-screw is fitted into the wall of the metal case for regulating the filling and emptying of the liquid from the pipet. The scale division of the micro-pipet is 0.001 ml.

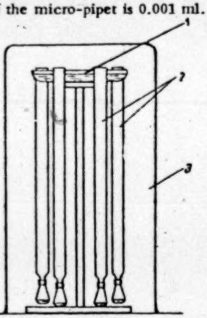

Fig. 1. Paper chromatographic separation of sugars:
1) solvent; 2) paper strips;
3) glass cover.

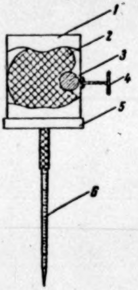

Fig. 2. Pipet:
1) case; 2) rubber bulb;
3) metal ball; 4) micro-screw; 5) cover of the thread; 6) micro-pipet.

The paper strips are fitted in a strictly perpendicular position after the drops of test solution have been applied to them. The top end to which the test sample is applied is immersed in the solvent so that the spot made by the sample is not less than 2 cm from the solvent surface. The lower end of the strip is placed in the neck of the flask so that its edge is firmly pressed to the wall. The chromatograms are run at a temperature of 18-22°.

TABLE 1

R_f Values for Various Sugars in a Solvent Consisting of Ethyl Acetate-Pyridine-Water (5 : 1 : 5)

Sugar	R_f
Galactose	0.15
Glucose	0.18
Mannose	0.22
Fructose	0.23
Arabinose	0.25
Xylose	0.33
Rhamnose	0.47

After the chromatograms have been run for 24 hours, five of the test strips are removed as well as the twelfth strip acting as indicator. The chromatograms are then dried and then one test strip is developed together with an indicator strip.

The developer is a solution of 1.66 g of phthalic acid and 0.92 ml of freshly prepared aniline in 100 ml ethanol. The dried chromatograms are moistened uniformly and then allowed to dry slightly in air, subsequently they are kept for 5 minutes in a drying oven at 105°.

Rhamnose and xylose are separated efficiently after 24 hours, accordingly, the amounts of these sugars are determined on the strips (the undeveloped ones) by the method described below.

After the chromatograms have been run for 50 hours, the remaining strips are removed and dried efficiently in air to remove solvent. One test strip and one indicator strip are developed. If separation has not proceeded far enough, as indicated by the chromatograms developed, they are run for a further few hours.

In establishing the nature of the sugars separated on the paper chromatograms, the color and position of the spots and the indicator strips are used as guides. On development with aniline phthalate, pentoses give colors ranging from rose to dark-red, depending on the amount of the sugars; hexoses give a brownish green color; rhamnose gives a brown color.

The relative positions of the spots are assessed on the basis of the R_f values of the sugars. Table 1 contains the R_f values of the sugars; these were determined by means of a solvent consisting of ethyl acetate, pyridine, and water (5 : 1 : 5).

Extraction of the Sugars from the Chromatograms

After chromatograms have been obtained, in which the necessary separation of the sugars has been achieved, (this is assessed from the developed indicator strip),they are completely dried in air and cut into parts, each of which contains the sugar to be determined. Sometimes, the arrangement of the sugars on different chromatograms from the same series of experiments is not the same, accordingly, when cutting the undeveloped chromatograms into separate parts, each of which should only contain one sugar, it is not enough to rely on the indicator strip alone.

In order to make sure that the requisite part of the chromatogram with only one sugar is being cut out, it is necessary to develop that part of the chromatogram adjacent to it . By making use of these supplementary indication, the position of the material which is being studied can be established with complete accuracy.

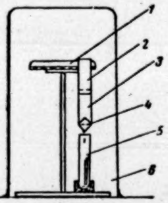

Fig. 3. Extraction of sugar from the chromatogram: 1) water; 2) filter paper; 3) chromatogram; 4) cover galss; 5) ebulliostat; 6) glass jar.

Extraction of the sugars from the chromatograms is carried out in a way similar to that used for running the chromatograms. Distilled water is used as the solvent. The piece of the chromatogram cut out is stuck by means of water to a piece of filter paper and to a cover glass as shown on Fig. 3. The solution of extracted sugar is collected in an ebulliostat, in which the sugar is subsequently determined quantitatively as described below. When the amount of extracted sugar is small (d = 3 cm) it is sufficient to collect 5-8 drops of liquid, while if the spot is large, then the time of extraction must be increased and the amount of liquid collected must be increased proportionally.

After the sugar has been extracted, the piece of the chromatogram is dried and developed in order to check that all the sugar has been extracted by the water.

Quantitative Determination of the Sugars Extracted from the Chromatograms

The micro-method used for determining the sugars extracted from the chromatograms is a modification of the ebulliostatic method developed by Nizovkin and Emel'ianova[10, 11]. The basis of this method is the direct titration of a hot copper-alkali solution with the sugar solution. In order to avoid the effect of atmospheric oxygen on oxidation of the sugars by the copper-alkali solution, the analysis is carried out in a special vessel - an ebulliostat. The titration end point is determined on the basis of the value of the oxidation — reduction potential of a platinum electrode immersed in the reactants.

The copper-alkali solution is made from equal volumes of two solutions: the first solution contains 2 g/liter of $CuSO_4 \cdot 5H_2O$, while the second contains 50 g/liter of potassium sodium tartrate, 75 g/liter of sodium hydroxide, and 0.08 g/liter of potassium ferrocyanide.

The setup used for determining the sugars is shown on Fig. 4. The reaction vessel — an ebulliostat — is a wide test tube inside which is fused a glass tube for leading in steam: above this is a side opening for the steam to pass out. The ebulliostat is supported on a cork in a flask containing boiling water. The opening in the top of the ebulliostat is sealed, during the time of the analysis, with a stopper into which are fitted a platinum electrode, one end of an electrolytic switch, and the tip of a micro-buret with a capacity of 2 ml and scale divisions of 0.001 mm. The other end of the electrolytic switch is connected to a lead chloride-amalgam electrode, which serves as the reference electrode. The lead chloride-amalgam electrode consists of a platinum disc immersed in a 10 % lead amalgam, which is covered with a saturated solution of lead chloride to which 2 % potassium chloride has been added. The potential of this electrode should be 440-450 millivolts with respect to the saturated calomel electrode. The electrodes are connected to a galvanometer.

Titration is carried out as follows. The sugar is extracted into the ebulliostat from the chromatogram, 2 ml of the first and second solutions is then added, the exact amount being measured out by means of a dosimeter (Fig. 5). The ebulliostat and reaction liquid are placed in the flask containing boiling water, and then sealed with the stopper into which the platinum electrode and electrolytic switch have been fitted in beforehand. The tip of the micro-buret is fitted into the free opening in the stopper, the micro buret being filled with a sugar solution of known concentration (about 0.02 %). After 2 minutes (hourglass) boiling, titration is started, the sugar solution being added from the micro-buret at the rate of 0.005 ml/second, until the galvanometer needle turns to zero. The buret tip is then removed from the stopper and the number of ml of sugar solution used for the titration established.

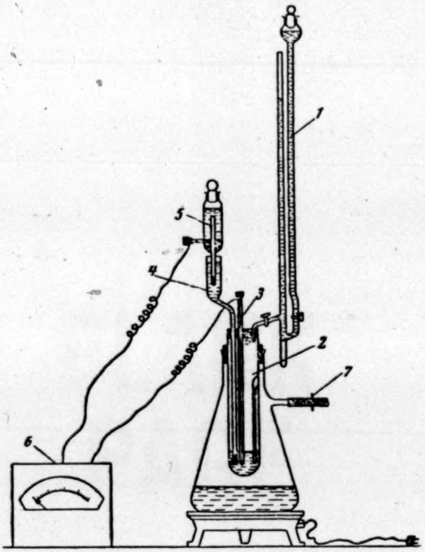

Fig. 4. Determination of sugar by a potentiometric ebulliostatic method:
1) micro-buret; 2) ebulliostat; 3) platinum electrode; 4) electrolytic switch; 5) lead chloride-amalgam-electrode; 6) galvanometer; 7) screw clip.

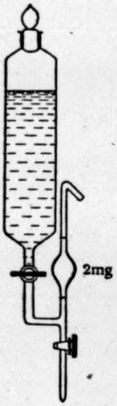

Fig. 5. Dosimeter.

Blank Test

Before an actual analysis of test material, a blank is carried out, in which the amount of sugar solution* used for titrating a solution in which the amount of sugar extracted from a chromatogram is zero. At the same time, the concentration of this solution of sugar is calculated by means of the following formaul: $T/V = a$ mg/ml, where T is the arbitrary titer of the copper-alkali solution; V is the amount in milliliters of sugar solution used for titration.

The Arbitrary Titer

The arbitrary titer of the copper-alkali solution is that amount of sugar used for reducing a known volume of copper-alkali solution of one concentration or another. Since the reducing capacity of various sugars differs, the titer of the copper-alkali soltuion should be established or calculated for each test sugar. For example, while the titer for glucose is 100, that for galactose is 107, while for arabinose it is 94.7, and for xylose it is 100, etc.

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* The most accurate analytical results are obtained when 10-15 % of the sugar taken for analysis is used up in the titration.

For the analysis of various amounts of sugars, it is necessary to use copper-alkali solutions containing different amounts of copper and potassium ferrocyanide. When the amount of sugar extracted from a chromatogram is not greater than 300 μg, 2 ml of the first solution containing 1 g/liter of $CuSO_4 \cdot 5H_2O$, and 2 ml of the second solution containing 0.4 g/liter of potassium ferrocyanide, 50 g/liter of potassium sodium tartrate, and 75 g/liter of sodium hydroxide, are used. When the amount of test sugar extracted from the chromatogram amounts to not more than 600 μg, the first solution used in this instance contains 2 g/liter of $CuSO_4 \cdot 5H_2O$, while the potassium ferrocyanide concentration of the second solution alone is increased to 0.8 g/liter.

When it is necessary to determine larger amounts of sugar, more concentrated solutions of cupric sulfate and potassium ferrocyanide must be used. The amount of cupric sulfate in the first solution can be increased to 0.8 g/liter; when this amount is used, up to 2500 μg of sugar can be determined.

Calculation

The sugar concentration of the test solution (hydrolyzate, sulfite liquor, etc.) is calculated by means of the following formula:

$$X = \frac{(T - ab) \cdot 100}{c \cdot 1000 \cdot 1000} = \frac{T - ab}{c \cdot 10^4}\ \%,$$

where T is the amount in milligrams of sugar used for reducing the copper-alkali solution taken for the analysis (the arbitrary titer); a is the sugar concentration of the solution used for titration, in mixrograms/ml; b is the amount in milliliters of the sugar solution used for titration; c is the number of milliliters of test solution taken for running the chromatograms; 10^6 is the conversion factor from micrograms to grams.

Results of Determinations Carried out by Means of the New Method

Synthetic mixtures of pure sugars, samples of wood hydrolyzates and sulfite liquors were analyzed by the method described above.

On Figs. 6, 7, and 8 are shown chromatograms obtained after various times of running the chromatograms. Table 2 contains analytical results obtained during analysis of chromatograms (mean of three determinations).

TABLE 2

Results of Sugar Determinations

Sample	Amount of reducing materials taken, in μg	Found, in μg						
		Glucose	Galactose	Mannose	Xylose	Arabinose	Other reducing materials	Total
Synthetic mixture 1	355	179	98	9	67	—	—	353
Synthetic mixture 2	433	100	10	—	275	44	—	429
Hydrolyzate 1	355	160	19	75	41	10	55	360
Hydrolyzate 2	469	207	56	60	40	38	59	460
Sulfite liquor 1	219	30	10	69	46	34	28	217
Sulfite liquor 2	180	26	12	60	40	28	18	184

The amount of recuding materials in the hydrolyzates, sulfite liquors, and synthetic mixtures taken coincides with the total amount of the individual sugars and other reducing materials.

SUMMARY

1. A new method has been developed for separating sugars by one-dimensional paper chromatography. This method permits separation of the reducing materials in wood hydrolyzates and sulfite liquors.

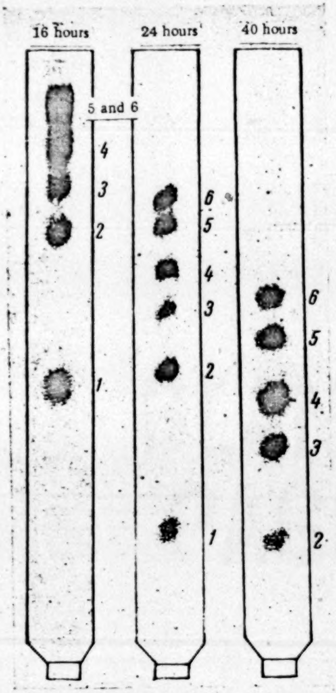
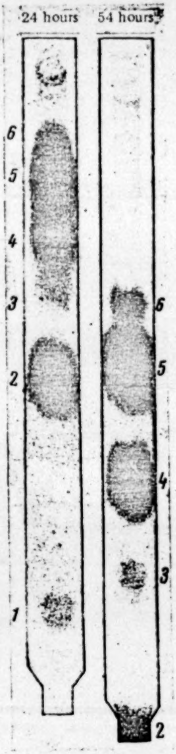

16 hours
24 hours
40 hours
5 and 6
4
3
2
1
6
5
4
3
2
1
6
5
4
3
2

Fig. 6.


24 hours
54 hours
6
5
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3
2
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2

Fig. 7.

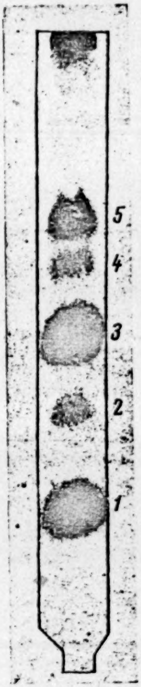

Fig. 8.

Fig. 6. Chromatograms for a synthetic mixture of six sugars at various stages during running of the chromatograms:
1) rhamnose; 2) xylose; 3) arabinose; 4) mannose; 5) glucose; 6) galactose.

Fig. 7. Chromatograms for wood hydrolyzate at various stages during running of the chromatograms:
1) rhamnose; 2) xylose; 3) arabinose; 4) mannose; 5) glucose; 6) galactose.

Fig. 8. Chromatograms for sulfite liquor after running the chromatograms for 48 hours:
1) xylose; 2) arabinose; 3) mannose; 4) glucose; 5) galactose.

2. A micro-method has been developed for the quantitative determination of sugar which have been separated by means of paper chromatography; 10 to 2,500 μg of sugar can be determined by this method with an accuracy of 2 μg.

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BRIEF COMMUNICATIONS

QUANTITATIVE DETERMINATION OF EUSINTOMYCIN

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Eusintomycin is the stearate of racemic 1-(paranitrophenyl)-2-dichloroacetamidopropanediole-1,3, or so-called sintomycin; it is obtained by the action of technical stearylchloride containing free stearic acid, thionyl chloride, hydrochloric acid, and elemental sulfur as impurities [1] on a solution of sintomycin in a mixture of dichloroethane and pyridine. Despite subsequent careful purification of the technical eusintomycin, small amounts of mineral chlorides, elemental sulfur, and uncombined stearic acid get into the pharmacopeia product, the amounts of these impurities are determined by methods outlined in the specifications governing production of this preparation.*

Two methods have been suggested for the determination of the amount of eusintomycin in a pharmacopeia product: one of them consists in determining free and combined stearic acid and calculating the difference as eusintomycin; in the second method eusintomycin is determined by first reducing its nitro group (zinc in hydrochloric acid), with subsequent diazotization of the amino product formed and calculating the amount of eusintomycin** on the basis of the amount of sodium nitrite used.

Since both the methods just mentioned are complicated, and take a long time to carry out, we have developed another method for the quantitative determination of eusintomycin in pharmacopeia preparations. It consists of the following.

First, the eusintomycin is extracted several times with water and the chloride ion determined by the Volhard method in the extract [2]; next the eusintomycin is reduced with Devarda's alloy in an alcoholic alkali solution. The organically combined chlorine is thereby converted into the alkali metal chloride, and this is determined together with the ionic chloride already present in the eusintomycin by the Volhard method. The difference between total chloride and the chloride determined by aqueous extraction gives the chlorine content of the eusintomycin, so that from this difference it is possible to calculate the percentage content of eusintomycin. The amount of impurities in pharmacopeia eusintomycin is determined by the usual methods, descriptions of which have already been given in the Departmental technical specifications mentioned above.

While developing this method we found that the stearic acid contained in the reduction products of eusintomycin interferes in the titration, since it is a surface-active material capable of forming stable suspensions of silver chloride and thiocyanate. In order to avoid errors during titration as a result of the presence of stearic acid, we added chloroform. The latter rapidly coagulates the silver salts mentioned, so that the solution being titrated clarifies, and titration is facilitated. We also noticed that the colored reduction products of eusintomycin interfere with titration. To destroy these materials we added hydrogen peroxide to the reaction solution, while for destroying excess peroxide we added ferrous sulfate.

Experimental results showed that reduction of eusintomycin by Devarda's alloy is quantitative, and that deviations in parallel tests do not exceed 1%. In special experiments we established that in order to effect complete reduction, it is necessary to use 4 parts by weight of Devarda's alloy to one part by weight of eustintomycin, for a reaction time of 30 minutes.

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* VTU (Departmental technical specifications) - 1955, USSR Ministry of Health.

** Archives, S. Ordzhonikidze All-Union Scientific Research Chem. Inst.

The method which we have developed for the quantitative determination of eusintomycin differs from the previous methods, in that while being simple and requiring a short time for execution it still gives results which are accurate enough to warrant its successful use for controlling production of eusintomycin.

Determination of Chloride Ions in Eusintomycin (Expressed in terms of Hydrochloric Acid). About 2-3 g of ground eusintomycin (weighed accurately) is placed in a 100 ml flask, and 50 ml of ice water added, the whole is shaken for 1 minute and then filtered. The same procedure is repeated a further three times. The combined wash liquors are placed in a conical flask and acidified with nitric acid; the chloride ions are then determined by titration with 0.1 N ammonium thiocyanate (indicator—ferric ammonium alum). A blank is carried out in parallel.

Determination of Percentage Content of Eusintomycin. About 0.25 g of carefully ground eusintomycin (weighed accurately) is placed in a 250-300 ml flask, and dissolved in 15 ml of alcohol by shaking in a warm water bath; 1 g of Devarda's alloy* is then added and the flask fitted with a reflux condenser; 40 ml of a 10 % chloride-free aqueous sodium hydroxide solution is added to the contents of the flask by pouring it through the condenser. If, on adding the alkali, a turbulent reaction sets in, the reaction mixture is cooled.

When the turbulent reaction has ceased, the mixture is boiled over a small flame for 30 minutes. 10-15 ml of butanol or isobutanol is added through the condenser to avoid foaming in the flask. The solution obtained is slightly cooled and filtered while warm through a plug of cotton wool into a 500-700 ml flask. The reaction flask and plug are washed with hot water until a negative reaction for chloride is obtained (test with silver nitrate) and the washings gathered with the main filtrate. 10-15 ml of 5 % hydrogen peroxide is added to the filtered solution, and the whole boiled for 5 minutes. After boiling the solution is cooled again and 50 ml of chloroform added, this is followed by nitric acid until the precipitate has dissolved; 25 ml of 0.1 N silver nitrate, 3 g of ferrous sulfate are then added and the mixture heated carefully for 10 minutes on a hot water bath. On cooling, the solution is titrated with 0.1 N ammonium thiocyanate (indicator—ferric ammonium alum); 1 ml of ammonium thiocyanate corresponds to 0.029481 g of eusintomycin.

A blank is carried out in parallel.

SUMMARY

A new, convenient method is described for the quantitative determination of eusintomycin in pharmacopeia products, which is suitable for production control.

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* Composition: 50 % Cu; 45% Al; 5% Zn.

A DISTILLATION METHOD FOR DETERMINING THE MOLECULAR WEIGHT OF ORGANIC COMPOUNDS

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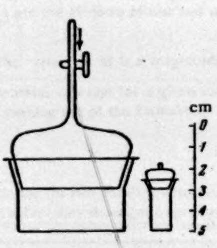
Lvov Polytechnical Institute

The principle of the distillation method of determining molecular weights may be outlined as follows. Solutions of small amounts of test material and a standard compound in the same solvent are kept in a vacuum together with pure solvent at a constant temperature until all the solvent has evaporated and equilibrium has been reached in the system. Since the vapor pressure of the solutions will be less than the vapor pressure of the pure solvent, then, after a certain time, the solvent will have evaporated completely, while the solutions will have been diluted, as a result of condensation of solvent, to such an extent that their vapor pressures will be identical. When equilibrium has been attained in the system, the solutions will have equal molar concentrations. Having determined the amount of solvent in the equimolar solutions, and knowing the molecular weight of the standard compound, it is possible to calculate the molecular weight of the test compound.



Apparatus for determining molecular weight.

The principle of this method of determining molecular weights was first used by Barger in 1904 [1], however, because of the complexity of the apparatus he suggested, this method has not found wide application. Some improvements have been suggested by Rast [2] in 1921, and Berl in 1930 [3]. Signer [4] suggested a more simple apparatus for determining molecular weights. Signer's apparatus consists of two glass bulbs connected by a wide U-shaped tube; a calibrated tube is fused to each bulb for measuring the volume, and each bulb is fitted with a side tube for filling it. An aliquot of a standard compound with a known molecular weight is introduced into one tube (for reference), while into the other bulb an aliquot of test material is introduced; the aliquots are then dissolved in a small amount of volatile solvent, a vacuum is set up in the system which is then sealed up and placed in a thermostat for a few days at a temperature of about 50°. By turning the apparatus, the solutions can be transferred into the calibrated tubes for measuring their volumes. The experiment is continued until complete equilibrium has been reached, i.e., until the volumes become constant. Having determined the equilibrium volumes, the molecular weight can be calculated. When such an apparatus is used, it is possible to get good results even for high molecular weight materials (molecular weights of about 8000). The drawback of this method, however, is the long time taken to carry out a determination (often more than a week). Further developments of this method have been aimed at improving the apparatus and cutting down the time required [5, 6].

In 1954, Childs [7] introduced an additional vessel containing pure solvent in order to speed up attainment of equilibrium. When this was done, results with an accuracy of up to 5 % were obtained in three days.

Experiments which we have carried out confirm the results obtained by Childs. However, when it is necessary to determine the molecular weight of a series of compounds, the work takes a long time. We decided therefore, while still using the same principle, to prepare an apparatus by means of which it should be possible to carry out simultaneous determination of the molecular weight of several materials. Instead of measuring the volume of the equimolar solutions, which would require a very complicated apparatus, we decided to weigh the equimolar solutions. For this purpose, we constructed the apparatus shown in the diagram; it consists of a wide necked cup which is sealed with a closely fitting ground glass stopper, the latter ending in a gas-outlet tube with a tap. 7-8 small test tubes with ground glass stoppers are placed in the cup. Test tubes and stoppers are numbered.

Determinations are carried out by introducing an aliquot of a standard material into one of the test tubes, while aliquots of test materials are placed in the others; the weights of the aliquots are 10-30 mg. The weights of the aliquots taken are approximately proportional to the molecular weights. The test tubes with their various aliquots of test materials are placed in the vessel without inserting their stoppers and 0.2-0.3 ml of acetone pipetted into each of them, 3-4 ml of acetone is placed on the floor of the vessel. The cup is then stoppered and the air evacuated from the vessel through the gas-outlet tube until the acetone on the bottom of the cup starts to boil. The tap is closed and a rubber cap fitted onto the gas-outlet tube, while a rubber ring is fitted around the edge of the ground glass joint; the apparatus is then placed in a thermostat at 40°. The apparatus is kept at this temperature until all the solvent has evaporated from the floor of the cup (about three days). The apparatus is then removed from the thermostat and the tap carefully opened so that the inrush of air does not destroy the equilibrium of the solutions, the test tubes are removed and rapidly stoppered, using forceps with rubber tips for this purpose. Since this operation takes 15-20 seconds, and the tubes are in an atmosphere saturated with solvent vapor, the evaporation rate is insignificant, and the equilibrium is not destroyed as a result of nonuniform evaporation of the solvent from the various solutions. The stoppered test tubes are weighed, the weights of the test tube plus aliquots are subtracted, and the weight of solvent in each tube calculated.

The molecular weight is calculated by means of the formula

$$M_x = \frac{a \cdot b}{b \cdot a} M, \quad \frac{a_x}{b_x} \cdot M \frac{b}{a},$$

where M_x is the molecular weight of the test compound; M is the molecular weight of the standard material; $\underline{a_x}$ and $\underline{a}$ are the aliquots of test and standard materials respectively; $\underline{b_x}$ and $\underline{b}$ the weights of the solvent in each case.

The ratio $\frac{b}{a}$ M is a magnitude which is the inverse of the molar concentration of the standard material, which remains constant for a given experiment. Consequently, calculation of the molecular weight can be simplified by making use of the formula

$$M_x = K \frac{a_x}{b_x}, \quad \text{where } K = \frac{b}{a} \cdot M.$$

Results for two parallel determinations of the molecular weight, using benzoic acid as the standard, are given in the Table; they show good agreement between each other; the error does not exceed 5 %.

Test sampe	Molecular weight of the sample	Molecular weight determined, using benzoic acid as the standard	Error, in %
Para-phenylenediamine	108	106	1.8
		106	1.8
Resorcinol	110	107	2.7
		113	2.7
Acetanilide	135	130	3.7
4,4'-Dihydroxydiphenylsulfone	250	134	0.7
	318	241	3.6
Phenolphthalein		251	0.4
		328	3.1
		325	2.2

Other volatile solvents can be used instead of acetone for molecular weight determination by this method. By increasing the size of the apparatus, it is possible to increase the number of test samples for molecular weight determination.

SUMMARY

1. An apparatus and a method are suggested for the simultaneous determination of molecular weight of a series of organic compounds, based on the principle of isothermal distillation.

2. The method gives results with good reproducibility; the experimental error does not exceed 5 %.

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ANNOUNCEMENT

The Commission on Analytical Chemistry of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR intends to call a conference in Moscow in June 1958, on the analysis of gases in metals.

It is intended that reports on the following questions be read and discussed at this conference:

1. The effect of gases on metal properties.

2. The physicochemical bases of modern methods of determining gases in metals (diagrams of state for the most important gas-analytical systems, the form in which the gases are found in the metals, adsorption and absorption, diffusion, thermodynamics of solution, and removal of gases from metals).

3. Determination of gases in metals (methods: vacuum fusion, chemical, reduction and oxidation, spectrographic, radioactivation, isotopic dilution, phase analysis; express methods and technological samples).

4. New apparatus for determination of gases in metals.

5. Unification of methods for analysis of gases in metals and preparation of standard samples.

The Commission invites workers in scientific research institutes, higher educational establishments, and factory laboratories to participate.

Subjects of reports to be read and annotated reports (4-5 typewritten sheets), as well as application for tickets should be sent to the Organizing Committee before April 1st 1958 (Moscow, B-49, P/ Ia 3085).

The exact date of the conference will be announced later.

Organizing Committee

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1) A new indicator "Caltsion IREA", for the complexonometric determination of calcium, has been synthesized at the All-Union Scientific Research Institute of Chemical Reagents (IREA); this indicator is superior to murexide with respect to the stability of its solution, color change contrast on interacting with calcium, and simplicity of use; 2) a new reagent "Pliumbon IREA" has also been synthesized for the photometric and complexonometric determination of lead. This reagent, is as sensitive and selective as dithizone and simpler to use.

Anyone wishing to test these new reagents may obtain a free sample, with instructions for use, by applying to the Institute of Chemical Reagents (Moscow, Zh-33, Samokatnaia Ul. D. 4a).

These reagents are not, at present, being produced on a factory scale; in order therefore to help the Institute to decide whether it is worthwhile to produce these reagents on a large scale, it is requested that all those interested should send their requrests for these reagents to the Institute within two months.

The Institute will advise on all questions relating to the use of Caltsion IREA and Pliumbon IREA.

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SORPTION OF MOLYBDENUM AND RHENIUM FROM VARIOUS MEDIA ONTO THE ANION EXCHANGE RESIN EDE-10, AND THE CHROMATOGRAPHIC SEPARATION OF THESE ELEMENTS

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Rhenium, being one of the most scattered elements, does not form its own characteristic minerals and as a result of its physicochemical affinity with molybdenum, it is always associated with the latter in the natural state. Because of the similarity in their chemical properties, separation of rhenium and molybdenum is a difficult problem. All the same, differences in the stability of their various valency states do permit one to separate them from each other. Quite a few methods have already been published on the separation of molybdenum and rhenium.

One of the first methods suggested was distillation of rhenium as $ReCl_7$ or Re_2O_7 [1, 2]: this method was subsequently improved [3, 4] and used for mass analyses [5, 6]. The following precipitants have been used either alone or in various combinations for separating these elements: 8-hydroxyquinoline [7] and α-benzoinoxime [8] for molybdenum, and hydrogen sulfide [9, 10] and nitron acetate [11] for rhenium. Electrolytic methods of separating these elements have been developed on the basis of differences in the reduction potentials of these elements [12, 13]. Many papers have been devoted to extraction separation of molybdenum and rhenium; these include: extraction separation of the compound formed between molybdenum and xanthogenate with chloroform [14, 15], extraction of molybdenum cupferronate with organic solvents [16], extraction with chloroform of the compound formed between rhenium and tetraphenylarsonium chloride [17, 18]. In recent years chromatographic methods have started to find use for separating these elements. Rhenium was first separated from molybdenum on Amberlite 4B [19]. Molybdenum, in the form of potassium molybdate, was eluted with a buffer solution of boric acid – NaOH at a pH of 8.35. Rhenium was eluted with 5% NaOH. Molybdenum and rhenium were later separated by the same authors on a charcoal adsorbent – Norite [20]. This pair of elements has also been separated by other investigators using sulfo-coal K [21], or a combination involving the use of alumina and sulfocoal K [22], and on Amberlite IRA-400 [23, 24]. In one of the latter cases, the molybdenum was eluted with 10% NaOH, and rhenium with 7 N HCl [23], while in the other, molybdenum was eluted with 1 N $K_2C_2O_4$, and rhenium with 1 M $HClO_4$ [24]. Very recently, Dowex-1 [25, 26] has been used for separating these elements.

In practically all the papers referred to above, in order to construct the elution curves, determination of the amount of molybdenum and rhenium in the filtrates has been carried out by normal analytical methods. Only in very few cases, for example as in [27], which dealt with the separation of rhenium and technetium, has use been made of the labelled atoms method whereby the separation process can be followed rapidly and accurately.

The work we have carried out on the chromatographic separation of molybdenum and rhenium was done with the aid of the Russian anion exchange resin EDE-10; this resin is characterized by high-exchange capacity, chemical stability, and mechanical stability, and can be used over a wide pH range. Studies were carried out under static conditions in HCl, HNO_3, H_2SO_4, and H_3PO_4, using the radioactive isotopes Re^{186} and Mo^{99}. The conditions which gave maximum differences in sorption of molybdenum and rhenium under static conditions were subsequently used for the separation of these elements in synthetic mixtures and natural objects on a column.

The behavior of rhenium and molybdenum on the anion exchanger EDE-10 under static conditions was studied as follows. Anion exchange resin which had been freed from mineral impurities by treatment with hydrochloric acid was converted into the chloride, nitrate, sulfate, or phosphate by eluting the resin with a 1-2 M solution of the appropriate acid. After the resin had been washed free of excess reagent with water, it was dried in air, and 250 mg aliquots of it weighed into 100 ml flasks. To each aliquot was then added 25 ml of one of the test acids in known concentration; this was followed by addition of radiochemically pure Mo^{99} and Re^{186} as indicators; these were added in the form of Na_2MoO_4 and $NaReO_4$ respectively in an amount of 0.1-0.2 ml. When equilibrium had been reached – after six to seven hours – during continuous agitation, aliquots were taken from each flask and transferred to targets which were then measured for their γ-radiation with an AMM-4 γ-tube.

TABLE 1

Sorption of Mo and Re from Various Acid Media

Acid concentration	HCl		HNO_3		H_2SO_4		H_3PO_4		
	% sorption						concentration, mole/liter	% sorption	
	Re	Mo	Re	Mo	Re	Mo		Re	Mo
pH 5	93.2								
pH 3		98	91.0	98.5	63.1	84.5			
pH 2		97.5	87.2	98.4	57.6	75.5			
0.001 g·eq/l									
0.01							0.01	95.0	98.0
0.1	69.5		68.6	92.5	24.8	46.0	0.1	76.0	97.4
0.5	17.4	90.8	38.7	54.6	20.1		0.5	50.0	88.8
1	15.9	25.2	28.3	35.1	16.6	30.0	1	23.7	83
2	16.6	17.6	17.7	10.8	17.0	20.2	2	4.2	72.8
3	17.0		10.5						
4	17.2	34.6	12.9	9.9	17.9	18.4	4	3.6	58.2
6	19.9	39.4	13.6	10.2	19.6	17.5	6	3.9	43.5
8	21.5	36.6	14.0	10.8	23	15.9	8	4.0	30.6
9		33.7		10.6					
10	19.1		15.6	12.9	23.2	21.0	10	8.5	26.4
12			14.6		24.4				

β-Radiation measurements were excluded on account of the absorptive effect of the media, particularly in the case of H_3PO_4 solutions. While in the case of HCl and HNO_3, the latter could be carefully removed by evaporation, when sulfuric acid was used we lost rhenium on evaporation because of the volatility of this element as Re_2O_7, and when H_3PO_4 was used, an absorptive layer was formed. Because of the insignificant amount of γ-radiation in the total spectrum of Re^{186}, we had to use a large amount of the latter in order to be able to carry out measurements based on γ-radiation.

Active preparations of Mo^{99} were measured using a lead filter 5.75 g/cm^2 thick [28]. The lead filter was used in order to exclude the effect of technetium radiation, since technetium is formed according to the reaction $Mo^{98}(n, \gamma)Mo^{99} \xrightarrow{\beta^-} Tc^{99m}$, and is found in equilibrium with molybdenum.

Knowing the activity of the indicator introduced and the activity still remaining in solution, the percentage sorption of molybdenum and rhenium was calculated for each concentration of test acid.

It follows from the results given in Table 1 that appreciable sorption of molybdenum and rhenium is only observed in hydrochloric, nitric, and sulfuric acid media up to concentrations of these acids of up to 0.1-0.5 N, while sharp differences in sorption between these elements, which could be used for their separation, were not observed throughout the whole concentration range of these acids.

The sharp differences in sorption of molybdenum and rhenium observed when phosphoric acid media are used (Figure 1) are connected, presumably, with the fact that molybdenum forms an anionic type complex which is readily sorbed by the anion exchange resin. Maximum differences are observed at a concentration of 2M of phosphoric acid; sorption of molybdenum amounts to 72.8% at this concentration, whereas that for rhenium is only 4%. This difference permits the use of phosphoric acid for separating molybdenum and rhenium under dynamic conditions, the rhenium being eluted with 2M H_3PO_4, while molybdenum is eluted with 10% NaOH. All tests under dynamic conditions were carried out on a 12-cm-long column, 5 mm in diameter. The same resin with a particle size of 100-150 mesh, and in the phosphate form was used. Before the column was loaded with

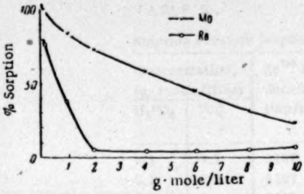

Fig. 1. Relation between sorption of Mo^{99} and Re^{186}, and H_3PO_4 concentration, on an EDE-10 anion exchange resin.

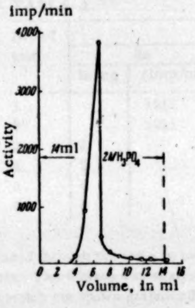

Fig. 2. Elution curve of Re^{186} with 2M H_3PO_4. Re^{186} added to the column had an activity of 5365 imp/min. Activity of the filtrate 5396 imp/min.

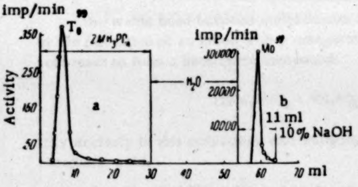

Fig. 3. Chromatographic separation of Tc^{99m} and Mo^{99}. Mo^{99} introduced onto the column, 49900 imp/min. Mo^{99} found in the filtrate, 49900 imp/min.

resin, the latter was washed with 2M H_3PO_4, an active preparation of Re^{186} in the form of sodium perrhenate was then transferred to the column; the amount introduced was 0.1-0.2 ml (5000-10,000 imp/min). Five to ten minutes after loading the column with rhenium, the latter was eluted with 2M H_3PO_4 at a rate of 0.07 ml/cm²/min. Individual portions of the filtrate were collected on targets which were then measured for their γ-radiation. When 14 ml of eluate had been collected, no activity could be detected on the target; elution was then stopped at this point.

From the results of activity measurements of the targets, an elution curve was constructed (Figure 2). Complete elution of Re^{186} was determined by adding up the activities of the targets and comparing the total activity with a standard. From the results given in Table 2 it can be concluded that Re^{186} was eluted quantitatively.

In order to establish the reason for the fact that rhenium is eluted in the first portions of the eluate, the sign of the charge on the rhenium passing into the eluate was determined by means of electrophoresis. It was found that all the rhenium taken in the form of Re^{186} collected at the anode; no activity could be detected at the cathode. Consequently, rhenium, despite the fact that it was in the state of an anion, i.e., in the form favorable for sorption on the anion exchange resin, nevertheless passed into the eluate.

It is obvious that rhenium has been eluted from the sorbent by phosphoric acid. In order to check on this assumption, distribution curves of rhenium between the anion-exchanger and phosphoric acid solutions were taken under static conditions, the phosphoric acid concentration being kept constant, but the phosphate ion content being varied by addition of Na_3PO_4. Five flasks containing weighed amounts of resin were taken and Re^{186} added, 25 ml of 0.1M H_3PO_4 was then added to each, and Na_3PO_4 added in such amounts that the total concentration of PO_4^{3-} in the five flasks was 0.1, 0.5, 1, 2 and 4M respectively.

When equilibrium had been reached, aliquots were taken and γ-radiation measurements carried out. As the results given in Table 2 show, sorption of rhenium falls with increasing PO_4^{3-} concentration. Consequently, in acid media, rhenium is found in the form of an anion which passes into the filtrate as a result of the competitive action of acid anions.

The same column was used for studying the behavior of Mo^{99} under the conditions used for eluting Re^{186}, i.e., during elution of a resin containing Mo^{99} with 2M H_3PO_4.

Since Mo^{99} and Tc^{99m} are found in equilibrium with each other, we studied their combined behavior during elution with 2M H_3PO_4. In view of the close similarity between the chemical properties of rhenium and technetium, one would expect that the latter will behave like the former. For these tests, the active preparation of Mo^{99} in the form of sodium molybdate containing Tc^{99m} was placed on an anion exchange resin and the column eluted with 2M H_3PO_4 as described for rhenium. 2M H_3PO_4

TABLE 2

Relation Between Sorption of Re^{186} and PO_4^{3-} Ion Concentration

Concentration, (g-moles/liter) H_3PO_4	Concentration, (g-moles/liter) PO_4^{3-}	Re^{186} introduced, in imp/min	Re^{186} found in the eluate, in imp/min	Re^{186} left on the resin, in imp/min	% Sorption
0.1	0.1	1107	286	821	74.5
0.1	0.5	1107	719	396	36.0
0.1	1	1107	891	216	19.5
0.1	2	1107	986	121	11.0
0.1	4	1107	1085	22	2.0

TABLE 3

No. of test	Added				Found			
	Re		Mo		Re		Mo	
	in mg	(imp/min)	in mg	(imp/min)	in mg	(imp/min)	in mg	(imp/min)
1		1211	2			1252	2.10	
2		1211	2			1285	2.12	
3	2			5953	2.01			5897
4	2			5953	2.08			5905
5	4		4		4.1		4.18	
6	4		4		4.08		4.2	

was passed through the resin in an amount equal to twice the volume of acid necessary for complete elution of rhenium. The filtrate was analyzed for the presence of activity by means of γ-measurements. The measurements which are shown graphically on Figure 3a showed that toward the end of rhenium elution, there was observed some activity. On the basis of tests carried out under static conditions, this activity could not be ascribed to Mo^{99} since the latter should be efficiently sorbed under these conditions. Accordingly, the peak on Figure 3a belongs to Tc^{99m}. In order to make sure of this, the activity was identified on the basis of its half-life period and the maximum energy of its β-radiation. Results of these identification tests showed that the half-life period of 6.44 hours and the values of the energy, shown on Figure 4, are in good agreement with published results [29] for Tc^{99m}. No other activity could be observed on washing the column with 2M H_3PO_4.

The stable bond between molybdenum and the anion exchange resin in the given instance can be explained by the formation of an anion with a comparatively high charge. Apparently, molybdate ions and phosphoric acid react to form a heteropoly compound:

$$12Na_2MoO_4 + 9H_3PO_4 \rightarrow H_7[P(Mo_2O_7)_6] + 8Na_3PO_4 + 10H_2O.$$

It is precisely in this connection that molybdate and perrhenate differ from each other in their interaction with phosphoric acid.

After 30 ml of 2M H_3PO_4 had been passed through the column containing molybdate, the column was washed with water until the filtrate gave a neutral reaction. The molybdenum was then eluted off the column with 10% NaOH. This is made possible by the fact that the heteropoly acid, in which form Mo^{99} is held by the column, is destroyed by the alkali. The reaction can be depicted as follows:

$$H_7[P(Mo_2O_7)_6] + 27NaOH \rightarrow 12Na_2MoO_4 + Na_3PO_4 + 17H_2O.$$

During elution of the column with alkali, the eluate, in individual portions, was collected on targets and analyzed for the presence of Mo^{99} by measuring the γ-radiation. 11 ml of 10% NaOH was used for complete elution of Mo^{99}. The elution curve shown on Figure 3b was constructed on the basis of the experimental results

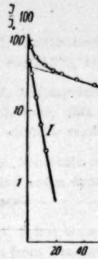

Fig. 4. Absorption of Tc^{99m} in aluminum: I) β-activity with an energy of 0.12 Mev; II) γ-activity.

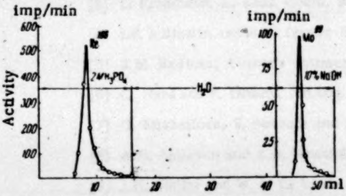

Fig. 5. Elution curves for indicator amounts of Re^{186} with 2M H_3PO_4 and a weighable amount of molybdenum (2 mg) with 10% NaOH.

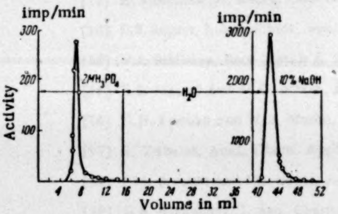

Fig. 6. Elution curves for weighable amounts (2 mg) of rhenium with 2M H_3PO_4 and for indicator amounts of Mo^{99} with 10% NaOH.

obtained. Completeness of elution of Mo^{99} was determined by adding up the activities of all the targets and comparing it with a standard. The results obtained indicated complete elution of Mo^{99}. Generalizing on the basis of all the results obtained, it can be stated that these elements are quantitatively eluted from the column by using 2M H_3PO_4 for eluting rhenium, and 10% NaOH for eluting the molybdenum.

The conditions established were used for separating synthetic mixtures of molybdenum and rhenium, and for isolating rhenium from natural objects. These elements were found in the following proportions in the synthetic mixtures used: 1) Re in indicator amounts, Mo in weighable amounts (2 mg); 2) Mo in indicator amounts, Re in weighable amounts (2 mg); 3) Re and Mo in weighable amounts (4 mg each). Elution of rhenium with 2M H_3PO_4 was controlled by Re^{186} activity and by means of the color reaction with $SnCl_2$ and KSCN, while for molybdenum the elution process was controlled on the basis of Mo^{99} activity and by the color reaction with potassium ethylxanthogenate. Elution curves for rhenium and molybdenum for cases 1 and 2 are shown on Figures 5 and 6.

The quantitative yield of indicator amounts of both elements was determined on the basis of the total activity in the appropriate portions of filtrate, while weighable amounts were determined on the basis of the reaction with nitron acetate in the case of rhenium [30, 31], and with lead acetate [32] for molybdenum (Table 3).

Of natural objects containing rhenium, we took molybdenite for testing.

Analysis of molybdenite for the purpose of isolating rhenium was carried out as follows. An aliquot of molybdenite contained in a conical flask was broken down with concentrated HNO_3 until all the molybdenum had been converted into molybdic acid. The white precipitate was dissolved in 10% NaOH in the same flask. The precipitated hydroxides of the heavy metals and undecomposed quartz were filtered off, and the filtrate acidified with phosphoric acid until the pH was 2. This solution was then passed through a column of EDE-10 20 cm long and 1 cm in diameter; the molybdenum was thereupon sorbed on the anion exchange resin while the rhenium was eluted by passage of 2M H_3PO_4 through the column at a rate of 2 ml/min. Completeness of removal of rhenium from the column was controlled on the basis of the disappearance of Re^{186} activity in the eluate, the Re^{186} having been added as an indicator, and by the disappearance of a color reaction with $SnCl_2$ and KSCN. An aliquot was then taken from the combined eluates and the rhenium content determined by the thiocyanate method [33, 34].

SUMMARY

1. Distribution of rhenium and molybdenum between the anion exchange resin EDE-10 and HCl, HNO_3, H_2SO_4, and H_3PO_4 solutions has been studied under static conditions using the radioactive isotopes Re^{186} and Mo^{99}.

2. A sharp difference was observed between the sorption of rhenium and molybdenum from phosphoric acid solutions; this can be explained by the fact that molybdenum, under these conditions, forms a complex anion which is readily sorbed by the active groups on the resin.

3. Synthetic mixtures of rhenium and molybdenum with varying proportions of the components have been separated under dynamic conditions; rhenium was eluted with 2M H_3PO_4 while molybdenum was eluted with 10% NaOH.

4. It has been shown that this technique can be used for isolating rhenium from molybdenites, and technetium from irradiated Mo samples.

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THE CHROMATOGRAPHIC METHOD IN QUALITATIVE ANALYSIS

IV. ANALYSIS OF CATIONS OF THE THIRD ANALYTICAL GROUP

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In the first article [1],material was presented which dealt with the establishment of adsorption series of cations and anions on the basis of their adsorbability on certain adsorbents, each group being taken separately. The second and third articles contained data obtained during a study of the development of chromatographic qualitative analysis of group IV and V cations on chromatographic alumina [2, 3].

The problem dealt with in the present article is development of a method for the chromatographic qualitative analysis of group III cations on chromatographic alumina.

The adsorption series of group III cations are arranged on adsorbents in the order indicated in Table 1.

TABLE 1

Adsorbent	Color of the adsorbent	Adsorption series
Chromatographic alumina	White	$Fe^{3+} = Cr^{3+} > Al^{3+} > Zn^{2+} > Co^{2+} = Ni^{2+} = Fe^{2+} > Mn^{2+}$
Permutite	White	$Fe^{3+} > Al^{3+} > Cr^{3+} = Zn^{2+} > Co^{2+} = Mn^{2+} = Fe^{2+} > Ni^{2+}$
Suifunite	Light yellow	$Fe^{3+} > Al^{3+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Fe^{2+} = Ni^{2+} = Mn^{2+}$
Sulfo-coal	Black	$Fe^{3+} = Cr^{3+} = Mn^{2+} > Co^{2+} = Zn^{2+} = Ni^{2+}$

The cations Fe^{3+}, Co^{2+}, Ni^{2+}, and Cr^{3+} can be detected directly on the adsorbents chromatographic alumina and permutite. Only Fe^{3+} cations can be detected on suifunite; the remaining cations form zones which are not clear cut with respect to color. Al^{3+}, Fe^{2+}, Mn^{2+}, and Zn^{2+} cannot be detected without additional development on the adsorbents.

Ni^{2+} cations can only be detected on chromatographic alumina when cobalt cations are absent in the solution, since, having equal adsorbabilities on the adsorbent indicated, the Ni^{2+} and Co^{2+} cations are adsorbed in the same zone. The same is true of Fe^{3+} and Cr^{3+}.

The limit of identification on alumina, without development, is 5.4 γ for Fe^{3+}, 35.0 γ for Co^{2+}, 35.0 γ for Ni^{2+}, and 30.0 γ for Cr^{3+}.

The cations were detected by the following technique. A test solution of the mixed cations of group III, mixed in equal volumes of solutions of equal concentration, was introduced by means of a pipet onto a chromatographic column 0.5 cm in diameter and 10 cm long packed with adsorbent. The chromatogram was washed with two to three drops of water, after which the developer was passed through the column. The adsorbed cations, located in different zones of the chromatogram, reacted with the reagent to give colored chemical compounds.

Experiments were carried out on columns packed with chromatographic alumina, permutite, suifunite, and sulfo-coal.

TABLE 2

Adsorbent	Appearance of the developed chromatogram
Chromatographic alumina	A 0.3 N solution of group III cations was passed through the adsorbent. The chromatogram was washed with 5-6 drops of water. In the upper part of the column a brown zone terminating in a grey-blue band was formed which indicated the presence of Fe^{3+} and Cr^{3+} ions; below, there was formed a rose-colored zone of a mixture of Co^{2+}, Ni^{2+}, and Fe^{2+} cations. The chromatogram was developed with a saturated solution of Na_2HPO_4. The grey-blue Cr^{3+} zone became wider, while underneath it was found the violet zone of $Co_3(PO_4)_2$.
The same	A saturated solution of Na_2HPO_4 was passed through the column packed with adsorbent; this was followed by the test solution. A light yellow zone of $FePO_4$ was found at the top of the column; this was followed by a grey-blue $CrPO_4$ zone, and a violet $Co_3(PO_4)_2$ zone. Detection of Cr^{3+} cations by this technique gave a more clearly defined chromatogram with respect to the color of the zone than the technique described above.
Permutite	Test solution was passed through the column, and the chromatogram washed with water. Formation of colored zones could be observed visually: at the top of the column was found the orange zone of Fe^{3+} ions, below this was a narrow, blue zone, and below this, in turn, a green zone. The chromatogram was additionally developed with a saturated solution of Na_2HPO_4. From top to bottom the zones were arranged as follows: a brown Fe^{3+} zone, a blue Cr^{3+} zone, a violet Co^{2+} zone, and a greenish Ni^{2+} zone.
Sulfunite	Test solution was passed through the adsorbent, and the chromatogram developed with a saturated solution of Na_2HPO_4. Characteristically-colored zones could not be obtained, since, on passing the test solution through the column, there was formed a light yellow zone which is the characteristic color of the damp adsorbent, and this masked the color of the phosphates of the remaining cations.
Sulfo-coal	No colored zones were formed on developing the chromatogram with Na_2HPO_4 solution.

As the results of experiments numbers 1 and 2 of Table 2 show, Cr^{3+}, Fe^{3+}, and Co^{2+} can be detected when all three are present simultaneously on one column, by any of the techniques indicated.

Detection of Cr^{3+} ions in the presence of Fe^{3+} by means of a saturated solution of Na_2HPO_4 was much better on columns treated beforehand with the developer, i.e., by using a combined technique of precipitation and ion-exchange chromatography; precipitation chromatograms were therefore studied.

With this aim in mind, experiments were carried out on the formation of precipitation chromatograms of the third-group cations. The carrier used was alumina, while the precipitant was Na_2HPO_4. Mixtures of carrier and precipitant were prepared in different proportions: 99:1, 95:5, 90:10, 75:25, and 50:50. Experiments were carried out using the same technique as that employed for the formation of ion exchange chromatograms. The column was packed with a dry mixture of carrier and precipitant, ground to have a particle size of 0.25 mm; five drops of the test solution were introduced onto the column; colored zones were formed.

Experimental results showed that the optimum mixture of precipitant and carrier for obtaining precipitation chromatograms in the form of phosphate precipitates was a mixture of 50% Al_2O_3 and 50% Na_2HPO_4. The colors of the zones were brighter, while the sensitivity of detection was greater. Cr^{3+} ions could be detected in solution at a concentration of 0.065 N. Sodium hydrophosphate forms a bright yellow-colored precipitate of iron phosphate with Fe^{3+} ions. Experiments showed that on using a mixture of 50% Al_2O_3 + 50% Na_2HPO_4, even at a concentration of 0.25 g · equiv/liter of the iron salt, a brown Fe^{3+} was not formed, because all the Fe^{3+} ions were bound by the precipitant as the light yellow $FePO_4$; accordingly it was found possible to observe the grey-blue zone of $CrPO_4$ visually. Precipitation chromatograms have more clearly defined boundaries for the colored zones than ion exchange chromatograms. With decreasing concentration of the solution, the width of the developed zones decreased correspondingly.

Chromatograms of Group III Cations Developed With Ammonium Thiocyanate Solution

Five to six drops of a 0.3 N solution of a mixture of group III cations was passed through the adsorbent and, after washing with water, the chromatogram was developed with 2 N NH_4SCN solution. The results of these experiments are given in Table 3.

TABLE 3

Adsorbent	Appearance of the developed chromatogram (from top to bottom of the adsorbent column)
Chromatographic alumina	Blood-red zone of $Fe(SCN)_3$ gradually changing over into a brownish yellow zone (mixture of Fe^{3+} and Cr^{3+}). Violet-red zone of $Co(SCN)_2$. The $Co(SCN)_2$ zone, as a result of excess developer, gradually changed color to violet, characteristic of $(NH_4)_2[Co(CNS)_4]$.
Permutite	Blood-red zone of $Fe(SCN)_3$, yellow-brown zone with a green ring of Cr^{3+}; violet-rose zone of $Co(SCN)_2$.
Sulfunite	The zones in the chromatogram did not have clearly defined colors.
Sulfo-coal	No colored zones.

The results given in Table 3 show that the best chromatograms are those formed on alumina and permutite; these chromatograms permit detection of Fe^{3+}, Cr^{3+}, and Co^{2+} cations when they are all present together in solution.

Chromatograms of Group III Cations Developed With Alkali Solution

Detection of group III cations by means of alkali solution was carried out on various adsorbents: after passing a 0.3 N solution of group III cations through a column packed with adsorbent, the chromatogram was washed with water and developed with an alkali solution. The experimental results are given in Table 4. The best chromatograms for detection of Fe^{3+}, Co^{2+}, and Ni^{2+} are those obtained in experiments Nos. 1 and 2.

TABLE 4

Expt. No.	Adsorbent	Appearance of the developed chromatogram (from top to bottom of the adsorbent column)
1	Chromatographic alumina	A dark brown zone of $Fe(OH)_3$ was formed in the upper part of the column; below this was located a violet Co^{2+} zone; the zone of the Cr^{3+} ions was arranged in the form of a grey-blue band between Fe^{3+} and Co^{2+}. After a few hours a dark brown Mn^{2+} zone was found under the Co^{2+} zone; the manganese ions were in the form of Mn^{4+} ions which gradually acquired a black color. When chromatograms free from Mn^{2+} ions were developed with KOH solution, a brown zone was formed on top, while below this a violet zone of Co^{2+} ions was found. A black zone was not observed.
2	Permutite	Top – brown zone of $Fe(OH)_3$, below – violet Co^{2+} zone which gradually acquired a blue color. Below there was formed a green $Ni(OH)_2$ zone.
3	Sulfunite and sulfo-coal	No zones could be detected after development of the chromatogram with KOH.

Experiments were carried out on formation of chromatograms by the method of precipitation chromatography. The carrier used was anhydrous alumina, while the precipitant was sodium hydroxide; various mixtures were used with proportions of 9:1, 5:1, and 3:1. The test solutions were 0.25 N solutions containing from two to three cations of the third and fourth groups, which form colored zones with alkali.

The experimental results showed that precipitation chromatograms with brightly outlined zones were formed rapidly during filtration of the solution. The zones were arranged in order of the solubility products of the hydroxides. Fe^{3+}, Cu^{2+}, Co^{2+}, and Mn^2 could be qualitatively detected in each others presence by precipitation chromatography in the form of the metal hydroxides.

Chromatograms of Group III Cations Developed With a Rubeanic Acid Solution

Five drops of a solution of a mixture of group III cations were passed through a column of adsorbent, the chromatogram was then washed with two drops of water, and developed with a 1% alcoholic solution of rubeanic acid.

The results of these experiments, which are given in Table 5, show that the use of rubeanic acid as a developer permits the detection of Ni^{2+} and Co^{2+} when these ions are simultaneously present in a solution of a mixture of group III cations.

TABLE 5

Composition of solution	Appearance of the developed chromatograms (from top to bottom of the adsorbent column)
Cobalt nitrate	Brown zone.
Nickel nitrate	Violet zone.
Mixture of nickel and cobalt salts	Violet-red zone.
Salts of Mn^{2+}, Fe^{2+}, Al^{3+}, and Zn^{2+}	All the cations form colorless zones.
A mixture of the salts of Fe^{3+}, Co^{2+} and Ni^{2+}	Dark brown zone of iron cations (III), violet-red zone of cobalt and nickel cations, bordered below by a narrow violet band – the nickel zone.
A mixture of the salts of Fe^{3+} and Ni^{2+}	Dark brown zone of iron (III) cations, violet zone of nickel cations.
A mixture of the salts of Fe^{3+} and Co^{2+}	Dark brown zone of iron (III) cations, light brown zone of cobalt cations.

The limit of identification of Ni^{2+} and Co^{2+} ions was found to be 0.13 γ, while the minimum concentration was 1 : 1,154,000.

Similar chromatograms were obtained on suifunite, but the color of the zones was not so bright and the boundaries were not so clearly defined.

Chromatograms of Group III Cations Developed With Potassium Chromate Solution

A solution of the test cation was passed through the adsorbent and the chromatogram developed with 2 N K_2CrO_4.

The most characteristically colored zone was formed during the detection of manganese cations.

The experimental results (Table 6) show that the best chromatograms are formed when chromatographic alumina and permutite, treated beforehand with a solution of K_2CrO_4, are used as adsorbents.

Experiments were carried out on determination of group III cations by means of precipitation chromatography. Tests were carried out on columns consisting of anhydrous alumina as carrier and potassium chromate as precipitant; the ratios of the former to the latter chosen were 9:1, 3:1, 2:1, and 1:1. The best results were obtained with a mixture of 25% of K_2CrO_4 and 75% of anhydrous alumina.

Chromatograms of Group III Cations Developed With a Solution of Ammonium Tetrathiocyanatomercuroate

A solution containing Zn^{2+} and Co^{2+} cations was passed through the adsorbent, and the chromatogram developed with ammonium tetrathiocyanatomercuroate and nitric acid.

Table 7 shows that the best results are obtained for detection of Zn^{2+} ions when chromatographic alumina and permutite are used as adsorbents.

TABLE 6

Adsorbent	Appearance of the developed chromatogram
Chromatographic alumina	Test solution was passed through a column of adsorbent. The chromatogram was washed with K_2CrO_4 solution. On top of the column there was formed a bright brown zone of Fe^{3+} ions; this terminated in a green-brown ring of Cr^{3+} zones, while below this was a yellow zone. Beneath this zone was found a zone of Co^{2+}, Ni^{2+} and Fe^{2+} ions, and below this again a brown zone of Mn^{2+} ions. Formation of distinctly colored zones was only observed after a certain time, as the result of the conversion of Mn^{2+} to Mn^{4+}.
The same	The adsorbent was treated beforehand with a K_2CrO_4 solution; after 24 hours the test solution was passed through a column of this adsorbent. A black zone was formed in the lower part of the column. The chromatogram is better than in experiment No. 1.
Sulfunite	K_2CrO_4 solution was passed through a column of adsorbent; this was followed after 24 hours by the test solution. A dark brown zone was formed in the lower part of the chromatogram, manganese ions being probably present.
Sulfo-coal	No positive results were obtained.

TABLE 7

Expt. No.	Sequence in which the reagents are passed through the column of adsorbent	Appearance of the chromatograms on the adsorbents		
		chromatographic alumina	sulfunite	permutite
1	Saturated solution of Na_2HPO_4 + 4 drops of test solution + 2 drops of HNO_3 + ammonium tetrathiocyanatomercuroate.	A blue zone of Zn^{2+} ions is formed within 2-3 seconds.	A grey-blue zone whose boundaries were diffuse appeared after 5 minutes.	Blue Zn^{2+} zone appeared in 1-2 seconds.
2	4 drops of test solution + 2 N solution of HNO_3 + ammonium tetrathiocyanatomercuroate.	As in experiment No. 1.	Diffuse grey-blue.	The same
3	5-6 drops of test solution + 7-8 drops of ammonium tetrathiocyanatomercuroate + 2 drops of 2 N HNO_3.	Blue zone of Zn^{2+} ions formed in 2-3 seconds.	Blue Zn^{2+} zone after 2-3 minutes.	

When the techniques described in experiments Nos. 1 and 2 were used, on decreasing the concentration of Zn^{2+} and Co^{2+}, the zinc ions could no longer be detected at a concentration of 0.03 N, while when the technique described in experiment No. 3 was used, the Zn^{2+} ions could be detected at lower concentrations. The results show that Zn^{2+} can be detected in the presence of Co^{2+} ions at very low dilutions, namely at concentrations of the test solution of 0.00035 g·equiv/liter.

When no Co^{2+} ions are present in solution, it is necessary, before developing the chromatogram with $(NH_4)_2[Hg(SCN)_4]$, to pass one drop of a very dilute solution of a cobalt salt through the column. If Co^{2+} ions are present at a high concentration in solution – a fact which is readily apparent from the rose color of the solution – the solution should be diluted with water until the rose color of the solution is no longer visually observable; this diluted solution can then be tested for Zn^{2+} ions.

At high Co^{2+} concentrations, the latter may interfere with the detection of Zn^{2+} ions since cobalt forms a compound having a blue-violet color with $(NH_4)_2[Hg(SCN)_4]$, as a result of which Zn^{2+} may be mistakenly assumed to be present.

Co^{2+} ions can only be detected by means of $(NH_4)_2[Hg(SCN)_4]$ in the presence of HNO_3 at a concentration of 0.07 g·equiv/liter. At lower concentrations, Co^{2+} ions cannot be detected and the blue zone which appears on developing with $(NH_4)_2[Hg(SCN)_4]$ and HNO_3 belongs to zinc ions, which can be detected in solution at a concentration of 0.00035 g·equiv/liter in the presence of Co^{2+} in solution.

Chromatograms of Group III Cations Developed by Ammonium Hydroxide

A solution of a mixture of group III cations was passed through a column packed with chromatographic alumina, and after washing with water, the chromatogram was developed with 2 N NH_4OH. Experiments were carried out with solutions differing in composition from each other.

TABLE 8

Composition of solution	Adsorbent	Appearance of the developed chromatogram (from top to bottom of the adsorbent column)
Solution of a mixture of cobalt and nickel salts.	Chromatographic alumina.	Brown-violet zone of cobalt ammoniate, below which is a blue zone of nickel ammoniate.
Solution of a mixture of group III cations.	Chromatographic alumina and permutite.	Top – brown zone of ferric ions, followed by a brown-rose zone of cobalt ammoniate, and below this a blue zone of nickel ammoniate. The zone colors are brightest on permutite.
Solution of a mixture of group III cations but not containing Ni^{2+}.	Chromatographic alumina.	Top – brown zone of iron, followed by a brown zone of cobalt ammoniate.
Solution of a mixture of group III cations.	Sulfunite	The zone colors were not clearly defined; a blue Ni^{2+} was not observed.

The results given in Table 8 show that the best chromatograms, with respect to zone colors, are obtained on using chromatographic alumina and permutite.

Using chromatographic alumina, on which the adsorbability of Co^{2+} and Ni^{2+} ions is the same, it is possible to separate these elements as their complex ammoniates by using ammonia solution. Separation is based on the fact that cobalt ammoniate is adsorbed to a greater extent than nickel ammoniate; this corresponds to the adsorption series of the ammoniates established by Schwab $[Co(NH_3)_6]^{3+} > [Ni(NH_3)_6]^{2+}$.

Cr^{3+} ions can be detected at a concentration of 0.125 N, Ni^{2+} and Co^{2+} at 0.0125 N, and Fe^{3+} ions at 0.005 N.

On the basis of the results of the experiments described above a technique has been worked out for the chromatographic qualitative analysis of group III cations.

A Chromatographic Qualitative Method for the Analysis of Group III Cations (Fe^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+})

In order to detect Fe^{3+} and Mn^{2+} ions, the test solution is passed through a column containing a 2-3 cm layer of chromatographic alumina. The appearance of a yellow-brown zone characteristic of $Fe(OH)_3$ indicates the presence of Fe^{3+} ions in solution. Mn^{2+} ions are detected in the filtrate issuing from the column. Since Mn^{2+} ions have such a low adsorbability, they are readily detected in the first drops of the filtrate by the reaction on filter paper with benzidene in ammoniacal solution.

Mn^{2+} can be detected directly on the adsorption column in the absence of Co^{2+} ions; for this purpose a column is prepared which contains a mixture of chromatographic alumina and potassium chromate with a particle size of 0.25 mm in the weight ratio of 3:1; the test solution is passed through this column. The formation of a dark zone in the lower part of the chromatogram, which gradually acquires a black color, indicates the presence of Mn^{2+} ions in the test solution. In addition, Mn^{2+} ions can be detected by passing the test solution through chromatographic alumina treated beforehand with three to four drops of concentrated alkali solution.

Formation of a dark brown zone which gradually turns black, and is located under the rose-colored zone of Co^{2+} ions indicates the presence of Mn^{2+} ions.

In order to detect Cr^{3+}, Co^{2+}, Ni^{2+} and Zn^{2+}, three to four drops of test solution are passed through a column of chromatographic alumina treated beforehand with five to six drops of a saturated solution of sodium hydrophosphate. In the upper part of the column is formed a white (with a hardly detectable yellow shade) zone of iron phosphate; below this is arranged the grey-green zone of chromium phosphate; this is followed by a rose-violet zone of cobalt phosphate.

In order to detect zinc ions a solution of $(NH_4)_2[Hg(SCN)_4]$ and two drops of 2N HNO_3 are passed through the column. A bright blue zone of Zn^{2+} ions is formed between the grey-green zone of the Cr^{3+} ions and the rose-violet zone of Cl^{2+} ions; the Zn^{2+} zone is in the form of a white precipitate of $Zn[Hg(SCN)_4]$ colored blue as the result of the presence of insignificant amounts of Co^{2+} ions. When no Co^{2+} ions are present, a fact which is readily established by the absence of a rose-violet colored zone in the primary chromatogram, it is necessary to pass a drop of a very dilute cobalt solution through the chromatogram before development with ammonium tetrathiocyanatomercuroate. When the test solution contains a large amount of Co^{2+} ions, which is evident from the rose color of the solution, then before the test it is essential that the solution be diluted with water until no rose color can be visually detected; at this point the solution can be tested further.

TABLE 9

Test solution	Developer	Limit of identification in γ, on 5 drops	Minimum concentration
$Fe(NO_3)_3$	Without developer	5.03	1:30000
$Co(NO_3)_2$	"	33.15	1:4000
$Cr(NO_3)_3$	"	9.62	1:15000
$Cr(NO_3)_3$	Sodium hydrophosphate	4.68	1:32000
$Co(NO_3)_2$	"	16.35	1:9200
$Fe(NO_3)_3$	Ammonium thiocyanate	10.33	1:14000
$Co(NO_3)_2$	Ammonium thiocyanate, concentrated solution	7.96	1:19000
$Mn(NO_3)_2$	Potassium chromate	3.71	1:40000
$Fe(NO_3)_3$	Sodium hydroxide	5.03	1:30000
$Co(NO_3)_2$	"	7.93	1:19000
$Mn(NO_3)_2$	"	0.91	1:160000
$Cr(NO_3)_3$	"	4.68	1:32000
$Fe(NO_3)_3$	Potassium ferrocyanide	2.51	1:60000
$FeSO_4$	Ferricyanide	0.21	1:710000
$Co(NO_3)_2$	Potassium ferrocyanide	1.98	1:76000
$Co(NO_3)_2$	Rubeanic acid	0.13	1:680000
$Ni(NO_3)_2$	"	0.13	1:680000
$ZnCl_2$	Ammonium tetrathiocyanatomercuroate + HNO_3	0.12	1:1250000
$Fe(NO_3)_3$	Concentrated ammonium hydroxide	2.51	1:60000
$Ni(NO_3)_2$	"	33.00	1:4500
$Co(NO_3)_2$	"	16.35	1:9200

In order to detect Ni^{2+} ions, four to five drops of test solution are passed through the column, and the chromatogram developed with ammonium hydroxide solution; the cobalt zone acquires a brown-violet color, while below this appears the blue zone of Ni^{2+} ions in the form of nickel ammoniate.

Ni^{2+} ions can be detected by development of the chromatogram with ammonia, after development of Zn^{2+} ions with ammonium tetrathiocyanatomercuroate in a second column. In the presence of sodium permutite, Ni^{2+}

can be detected by the formation of a green zone in the primary chromatogram, this zone being located below the rose-violet zone of Co^{2+}.

Ni^{2+} and Co^{2+} can also be detected by means of rubeanic acid. The reaction is very sensitive and permits detection of Ni^{2+} and Co^{2+} in amounts down to 0.13 γ during analysis with two drops of the test solution. In this case, two to three drops of test solution are passed through chromatographic alumina, and the chromatogram developed with rubeanic acid. When Ni^{2+} and Co^{2+} are present, there is formed a red-violet zone; when Co^{2+} ions are present while Ni^{2+} are absent, there is formed a brown zone of cobalt rubeanate in the form of an inner complex salt.

When Ni^{2+} is present and Co^{2+} absent, a blue-violet zone of nickel rubeanate is formed. Thus, the presence or absence of these two ions can be established on the basis of the color of the zone obtained.

Detection of Al^{3+} and Fe^{2+} is carried out directly on the test solution by means of spot reactions [4]. A complete analysis takes eight to ten minutes.

TABLE 10

Expt. No.	Method	Concentration, in g·equiv/liter	Amount of test solution taken for analysis, in ml	Time, in min, for carrying out an analysis	Experimental results
1	Macro method	0.0312	5	180	All cations were detected readily.
2		0.0156	5	160	Ni^{2+}, Co^{2+}, Al^{3+}, and Zn^{2+} detected very poorly.
3	Semi-micro method	0.0312	1	57	All cations were detected readily.
4		0.0156	1	45	Further dilution of the solution led to poor results.
5	Spot method	0.0312	1	20	All cations were detected readily.
6		0.0156	1	20	Further dilution of the solution led to poor results.
7	Chromatographic method	0.0312	0.5	8	All cations were detected readily.
8		0.0156	0.5	8	
9		0.0078	0.5	10	

Experiments were carried out in order to establish the sensitivity of reactions [5, 6] for group III cations with various reagents on chromatographic alumina. The results obtained are given in Table 9.

Experiments were also carried out on a comparative evaluation of various methods of detecting group III cations in solution.

Results of these experiments are given in Table 10. They demonstrate that the chromatographic method of analyzing group III cations has a number of advantages as compared with other methods. It only takes 8-10 minutes to carry out a chromatographic analysis of these cations, as against 20 minutes to 3 hours for the other methods. Chromatographic analysis can be carried out on a very small volume of test solution, and the amount of reagent used is 20-40 times less than that required for the macro and semi-micro methods.

The results of experiments Nos. 2, 4, 6, and 9 (Table 10) show that the chromatographic method is more sensitive than the others.

SUMMARY

1. It has been demonstrated that group III cations can be detected chromatographically when they are

present simultaneously in solution; they are detected on adsorbents – chromatographic alumina, permutite, and sulfunite – by means of various developers and precipitants.

A comparison of precipitation chromatograms with ion-exchange chromatograms showed that there was hardly any difference in the colors of the zones obtained. Nevertheless, precipitation chromatograms exhibit more clearly defined colored-zone boundaries.

2. A technique has been developed for the chromatographic qualitative analysis of group III cations, present together in solution, in which the adsorbent used is chromatographic alumina. Chromatographic analysis of group III cations can be carried out in the course of eight to ten minutes.

The limit of identification of each group III cation has been established for development on chromatographic alumina.

3. Various methods of detecting group III cations in solution have been compared. The chromatographic method is more rapid; it can be carried out with small amounts of reagents and minimum amount of test solution; it is also more sensitive than the other methods.

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THE APPLICATION OF PRECIPITATION CHROMATOGRAPHY ON PAPER FOR ANALYSIS OF INORGANIC CATIONS

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In an article published earlier [1] the possibility was demonstrated of using precipitation chromatography on paper as a spot variant in the qualitative analysis of inorganic cations. The present article contains results of investigations connected with an attempt to solve some problems in the theory of precipitation chromatography. Results are also given regarding the conditions for using this method for the analysis of inorganic cations (the values for the limits of identification in relative proportions).

Considerable attention has been given to a study of the effect of a series of factors on the development of the zones of the precipitates of individual cations. In carrying out these studies we pursued the aim of studying the possibilities of using precipitation chromatography as a method for determining the comparative solubility of precipitates, and also for establishing sorption series on the basis of the relative dimensions of the precipitation zones of individual cations. The main object was to establish the regularities between the width of the precipitate zone of various ions and the magnitude determining the zonal displacement and completeness of separation of the components of a test solution, which is one of the problems in the theory of precipitation chromatography.

1. The Relation Between the Dimensions of an Individual Cation Precipitation Zone and the Value of the Solubility Product of the Given Precipitate

In order to establish this relation, formation of the precipitates of individual cations was studied. 0.1 N solutions of the nitrates of the cations which one normally meets in the practice of qualitative analysis were used for the work. The volume of the drop of test solution was 0.025 ml. The concentration of the precipitant was calculated on the basis of the law of equivalence and the law of the conservation of matter.

In succession, the primary, washed, and developed chromatograms were prepared according to a technique described previously [2].

From a study of the formation of the precipitates of individual cations, it was established that:

1) The final zone dimensions of an individual cation precipitate were assumed by the washed chromatogram and not by the primary chromatogram.

2) On washing the primary chromatogram with solvent, the dimensions of the precipitation zone at first increased and then, after five to six washings, stabilized despite the further action of the solvent.

3) The final dimensions for the precipitation zones of individual cations, obtained on paper impregnated with the same precipitant, differed from each other and were found to exhibit a direct proportionality to the values of the solubility products of the precipitates formed.

Further experiments established a relation between these values, which could even be expressed in quantitative terms.

It was found, other conditions being equal, that the dimensions of the precipitation zones of two separate cations on a washed chromatogram were inversely proportional to the indices of the solubility products of the given precipitates.

It should be pointed out that those values of the solubility products, the relative values of which determine the concentration of the test ions in the saturated solution above the precipitate, and on the ratios of which (according to the solubility product) the zonal distribution of the precipitates on the chromatogram depends, corresponded to this condition.

We should like to point out that the ratio of the dimensions of the precipitation zones of two individual cations on a washed chromatogram characterizes the relative mean rate of movement of the precipitates (the path traced by the precipitated ion during formation of a washed chromatogram).

Taking this fact into account, and designating the relative mean rate of movement of the precipitates by K_b, we can express the final relationship as follows

$$K_b = \frac{d_{M^+A^-}}{d_{K^+A^-}} = \frac{pL_{K^+A^-}}{pL_{M^+A^-}}, \qquad (1)$$

where d_{M+A^-} and d_{K+A^-} are the diameters of the precipitation zones corresponding to the least and most soluble compound respectively, and pL_{M+A^-} and pL_{K+A^-} are the indices of the solubility products of these compounds.

The establishment of a relation between the width of the precipitation zone of an individual cation and the solubility product of this compound permits one to:

1) assess the comparative solubility of precipitates formed on a chromatogram on the basis of the relative dimensions of the precipitation zones on a washed chromatogram;

2) establish the solubility series of precipitates by a chromatographic method, by making use of the direct relation between these values;

3) choose, deliberately, the precipitant and optimum conditions for the chromatographic separation of mixtures by means of a precipitation mechanism.

By studying the chromatograms of twin separations it was found possible to establish the numerical value of the coefficient K_b, by means of which it was possible to separate mixtures in the form of precipitates. It was found that a pair of inorganic cations can be separated by means of precipitation chromatography on paper, as long as the value of the coefficient K_b does not exceed 0.75. This corresponds to an interval in the values of the solubility products of the precipitates of the ions to be separated, of about three orders of units.

Further work showed that those ions which can be separated when present in pairs, can also be separated from more complicated mixtures. The zonal distribution of the components of a complex mixture on a precipitation chromatogram and the completeness of separation of this mixture, as tests have shown, are also determined by the value of the coefficient K_b.

It may be said that K_b, the coefficient of the mean relative rate of movement of the precipitate, has the same significance in the theory of precipitation chromatography as the R_f value has in partition chromatography.

2. The Chromatographic Solubility Series of Precipitates

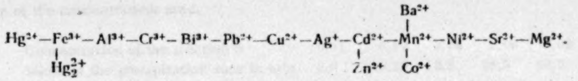
Using the direct relation between the width of the precipitation zone of a single cation on a washed chromatogram and the value of the solubility product of the given precipitate, chromatographic solubility series of precipitates were established on paper which had been treated with: sodium arsenite, sodium hydrophosphate (the disodium salt), potassium iodide, sodium silicate, thiourea, potassium ferrocyanide, and potassium chromate.

The series obtained differed from one another according to the nature of the precipitant. These series, which are given below, are arranged in order of increasing solubility of the precipitates.

1. The series obtained on a paper impregnated with sodium arsenite

$$\begin{array}{l} Hg^{2+}-\underset{\overset{|}{Hg_2^{2+}}}{Fe^{3+}}-Cr^{3+}-Bi^{3+}-Al^{3+}-Cu^{2+}-Pb^{2+}-Ag^{+}-Cd^{2+}-Zn^{2+}-\underset{\overset{|}{Ni^{3+}}}{Co^{2+}}-Ba^{2+}-Sr^{2+}. \end{array}$$

2. The series obtained on a paper impregnated with sodium hydrophosphate (disodium salt)

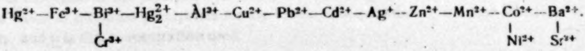


$$Hg^{2+}-\underset{\substack{|\\ Hg_2^{2+}}}{Fe^{3+}}-Al^{3+}-Cr^{3+}-Bi^{3+}-Pb^{2+}-Cu^{2+}-Ag^{+}-\underset{\substack{|\\ Zn^{2+}}}{Cd^{2+}}-\overset{\substack{Ba^{2+}\\ |}}{\underset{\substack{|\\ Co^{2+}}}{Mn^{2+}}}-Ni^{2+}-Sr^{2+}-Mg^{2+}.$$

3. The series obtained on a paper impregnated with potassium iodide

$$Ag^{+}-Hg^{2+}-Hg_2^{2+}-Bi^{3+}-Cu^{2+}-Pb^{2+}.$$

4. The series obtained on a paper impregnated with sodium silicate

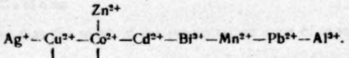


$$Hg^{2+}-Fe^{3+}-\underset{\substack{|\\ Cr^{3+}}}{Bi^{3+}}-Hg_2^{2+}-Al^{3+}-Cu^{2+}-Pb^{2+}-Cd^{2+}-Ag^{+}-Zn^{2+}-Mn^{2+}-\underset{\substack{|\\ Ni^{2+}}}{Co^{2+}}-\underset{\substack{|\\ Sr^{2+}}}{Ba^{2+}}.$$

5. The series obtained on a paper impregnated with thiourea

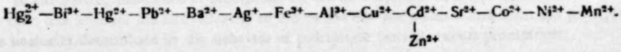
$$Hg_2^{2+}-Ag^{+}-Cu^{2+}-Hg^{2+}-Bi^{3+}-Pb^{2+}-Cd^{2+}-Zn^{2+}-Cr^{3+}-Fe^{3+}-Nn^{2+}-Mn^{2+}-Co^{2+}.$$

6. The series obtained on a paper impregnated with potassium ferrocyanide



$$Ag^{+}-\underset{\substack{|\\ Fe^{3+}}}{Cu^{2+}}-\overset{\substack{Zn^{2+}\\ |}}{\underset{\substack{|\\ Ni^{2+}}}{Co^{2+}}}-Cd^{2+}-Bi^{3+}-Mn^{2+}-Pb^{2+}-Al^{3+}.$$

7. The series obtained on a paper impregnated with potassium chromate



$$Hg_2^{2+}-Bi^{3+}-Hg^{2+}-Pb^{2+}-Ba^{2+}-Ag^{+}-Fe^{3+}-Al^{3+}-Cu^{2+}-\underset{\substack{|\\ Zn^{2+}}}{Cd^{2+}}-Sr^{2+}-Co^{2+}-Ni^{2+}-Mn^{2+}.$$

The value of these series, from the point of view of applying precipitation chromatography on paper in the qualitative analysis of inorganic materials, lies in the fact that they:

1) serve as an additional help in predicting the possibility of separating a complex mixture on the basis of the law of series. In accordance with this, members of the various series can be more readily separated from each other, the further apart they are in the series.

2) They reflect the comparative solubility of actual precipitates.

3) They facilitate the choice of precipitant. Choice of precipitant is an important link in separating mixtures by precipitation chromatography.

4) Establishment of the solubility series of precipitates by a chromatographic method is characterized by its simplicity and the speed with which it can be carried out: it facilitates development of an analytical scheme for ionized materials based on precipitation chromatography on paper.

3. The Effect of the Concentration of the Test Solution on the Development of the Size of the Precipitation Zone of a Single Cation

The original solutions used in the tests were those of the nitrates of the respective cations; solutions of the following strengths were used: 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 N. The volume of the drop of test solution placed on the paper was 0.025 ml. The concentration of precipitant used was the same as that used in experiments on establishing the relationship between the width of the precipitation zone and the value of its solubility product.

Primary, washed, and developed chromatograms were prepared in succession. The primary chromatogram was washed each time with five drops of distilled water until the precipitation zone reached its terminal size.

As an example there are given below the final dimensions of the precipitation zone of silver chromate as a function of the concentrations used.

Concentration of the solution N	0.01	0.02	0.04	0.06	0.08	0.1
Width of the precipitation zone in mm	8.0	10.35	12.5	14.5	16.5	18.5

The results obtained confirm that the equation published earlier [3] can be satisfactorily applied for separation by precipitation chromatography on paper by an ascending method:

$$d = d_0 + Kc, \tag{2}$$

where d is the width of the precipitation zone (in mm) at a given concentration of the original solution; d_0 is the zone width of the same precipitate for the lowest concentration of the test solution; K is a proportionality constant; and c is the concentration used.

The relation expressed by Formula (2) indicates the possibility of carrying out a quantitative determination of a single cation on the basis of the zone width of a precipitate of this cation on a washed chromatogram.

The proportionality coefficient K is determined graphically as the slope of a plotted curve.

4. The Effect of Other Factors on the Development of the Size of the Precipitation Zone of Separate Cations

Further work showed that the width of the precipitation zone of separate cations also depends on:

a) the volume (drop size) of test solution (direct relationship); b) precipitant concentration (inverse relationship; c) the nature of the precipitate formed (other conditions being equal, amorphous precipitates occupy wider zones than crystalline precipitates on washed chromatograms).

In calculating the effect of precipitant on the development of the precipitation zone of various ions, one must take into account the individuality of the cation and the anion which form the precipitate. This individuality is basically determined by the behavior of precipitate toward excess precipitant.

For precipitates which do not interact with excess precipitant,excess of the latter favors their complete separation on a narrower band. The zone boundaries of such precipitates are clearly defined.

In the case of precipitates which are capable of reacting with excess precipitant to form soluble complex compounds, excess precipitant leads either to diminution in zone size (as a result of its partial dissolution) or to complete dissolution of the precipitate formed.

Thus, a precipitate of mercuric iodide (the red modification) did not separate out at all on paper treated with 1% and 10% solutions of potassium iodide. On paper which had been impregnated with 4-5% precipitant solutions, while precipitates were formed, they dissolved appreciably during the process of preparing the washed chromatograms. The best-developed zone for this precipitate was obtained by using a 2% concentration of precipitant.

From what has been said, it follows that for complete deposition of precipitates which are capable of reacting with excess precipitant, the latter must be placed on the paper in amounts which are equivalent to the amounts of test cations.

5. The Effect of External Factors on the Formation of the Precipitation Zones of Individual Cations

Of the external factors which affect the development of the precipitation zones, the following were taken into account:

1) temperature changes; 2) the extent of physical adsorption; 3) the effect of other electrolytes; 4) interaction of test ion with solvent; 5) interaction of a given precipitate with other precipitates; and 6) pH changes in the medium.

It was found that temperature changes within the limits 10-30° do not lead to appreciable changes in the

TABLE 1

Reaction Sensitivity

Test cation	Limit of identification, in γ	Limiting dilution	Reagent used for developing the chromatogram	Test cation	Limit of identification, in γ	Limiting dilution	Reagent used for developing the chromatogram
NH_4^+	10.5	1 : 2400	Sodium-p-nitrophenylantidiazotate	Co^{2+}	0.75	1 : 33000	Rubeanic acid
K^+	40	1 : 625	Dipicrylamine	Ag^+	25.0	1 : 1000	Potassium chromate
Mg^{2+}	30	1 : 835	Magneson I	Hg_2^{2+}	20.0	1 : 1250	Thiourea
Sr^{2+}	12	1 : 2100	Sodium rhodizonate	Hg_2^{2+}	12.5	1 : 2000	Potassium iodide
Ba^{2+}	5	1 : 5000	Sodium rhodizonate	Pb^{2+}	14.0	1 : 1800	Sodium rhodizonate
Al^{3+}	5.5	1 : 4550	Alizarin	Pb^{2+}	6.5	1 : 3850	Potassium iodide
Cr^{3+}	2.4	1 : 10400	Benzidene	Hg^{2+}	25.0	1 : 1000	Potassium iodide
Fe^{3+}	1.0	1 : 25000	Potassium ferrocyanide	Bi^{3+}	4.5	1 : 5560	Thiourea
Mn^{2+}	0.35	1 : 71500	Benzidene	Bi^{3+}	12.5	1 : 2000	Potassium iodide
Zn^{2+}	0.3	1 : 83500	Dithizone	Cu^{2+}	2.5	1 : 10000	Rubeanic acid
Ni^{2+}	60	1 : 420	Thiourea	Cu^{2+}	2.5	1 : 10000	Dithizone
Ni^{2+}	3.0	1 : 8350	Rubeanic acid	Cd^{2+}	1.25	1 : 20000	Cadion
Co^{2+}	36	1 : 1700	Thiourea	Cd^{2+}	1.25	1 : 20000	Dithizone

development of the size of the precipitation zones of individual cations.

The part played by the paper in physical adsorption is completely insignificant. All the same, the effect of physical adsorption on the part of the other precipitate, in individual cases, has a considerable effect on establishment of the final dimensions of the precipitation zone of various cations. In such cases, the other precipitate, in fulfilling the role of a sorption column, holds the cation in the test solution by physical sorption forces during filtration of the solution through the layer of precipitant-sorbent.

As a consequence, the precipitation zone of the test cation will not develop as it should, because of incomplete precipitation of this cation in its layer.

Studies carried out with the object of establishing the effect of other electrolytes on the development of the size of the precipitation zones of individual cations, showed that this effect is insignificant.

The effect of the pH of the medium on precipitate formation was also of interest.

The experiments carried out along these lines led to the following conclusions.

Washing with dilute acids, of precipitates obtained on reaction paper and which are soluble under static conditions, did not, in most cases, lead to solution of the precipitates. Thus, an attempt to use the phosphate method of separating and identifying cations — which had been suggested by Petrashen' [4] as a test-tube method — for analyzing the same cations by the method of precipitation chromatography on paper, did not lead to the expected results. Precipitates which were soluble in acetic acid were not freed from precipitates which were only soluble in mineral acids.

This can be explained by the fact that during filtration of an acid solution through paper, a large fraction of the hydrogen ions is combined by adsorption

TABLE 2

Limiting Ratios

Test cation	NH_4^+	Mn^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	K^+	Sr^{2+}	Ba^{2+}	Pb^{2+}	Mg^{2+}	Al^{3+}	Fe^{3+}	Cr^{3+}	Ni^{2+}	Co^{2+}	Hg_2^{2+}	Bi^{3+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Ag^+	Hg_2^{2+}	Pb^{2+}	Hg^{2+}	Bi^{3+}
	Precipitant Na_2SiO_3					Precipitant Na_2HPO_4	Precipitant Na_3AsO_3			Precipitant $K_4[Fe(CN)_6]$			Precipitant NaCl	Precipitant			Thiourea				Precipitant K_2CrO_4	Precipitant KI			
	Developer																								
Accompanying cations	Sodium p-nitrophenylantidiazotate	Benzidene	Rubeanic acid			Dipicrylamine	Sodium rhodizonate			Magneson I	Alizarin	$K_4[Fe(CN)_6]$	Benzidene	Thiourea			Dithizone				K_2CrO_4	KI			
NH_4^+	1	60	400	1700	25	0.5	25	40	50	6	225	1330	346	25	60	35	285	2150	100	250	25	100	10	25	20
Na^+	12	3640	400	1700	500	15	70	120	100	30	225	1330	346	25	60	65	285	6450	500	875	50	100	200	50	100
K^+	12	3640	400	1700	500	1	70	125	100	30	225	1330	346	25	45	65	285	4300	500	500	50	100	40	50	50
Mg^{2+}	60	1820	100	20	100	10	14	30	20	1	25	665	60	12,5	20	32	150	4300	500	500	25	50	100	25	50
Ca^{2+}	120	1820	400	300	250	15	15	25	50	30	220	1330	24	40	60	65	285	6400	500	750	50	100	200	50	50
Sr^{2+}	120	1820	400	1700	500	30	1	25	50	30	120	1330	24	40	60	65	285	4500	475	900	50	100	200	50	100
Ba^{2+}	40	1270	136	580	175	10	14	1	35	15	75	470	10	10	20	22	100	1050	175	175	10	35	70	17.5	35
Al^{3+}	24	16	200	330	100	15	14	20	25	5	1	665	60	10	40	32	155	1075	250	500	25	50	100	25	50
Cr^{3+}	60	10	20	1	25	30	52	50	50	5	200	1330	1	5	35	65	285	10	500	500	10	100	200	50	50
Fe^{3+}	120	70	400	10	25	30	30	25	10	15	25	1	70	2	35	12	285	80	500	25	10	100	2	10	100
Mn^{2+}	35	1	200	1	100	20	23	15	10	5	30	1330	12	40	100	32	285	115	100	10	1	100	200	50	100
Zn^{2+}	60	1820	80	20	100	15	12	15	10	5	220	1330	70	1	20	65	285	1	100	25	50	100	200	50	100
Ni^{2+}	60	110	1	10	10	30	25	15	10	15	30	665	10	5	50	65	280	12	100	25	50	100	200	50	100
Co^{2+}	60	10	12	1	10	30	15	15	10	5	30	665	23	40	1	65	280	10	100	25	5	100	200	50	100
Ag^+	120	12	22	45	50	30	34	50	50	30	225	1330	115	40	70	65	25	2200	100	500	1	10.8	10	1	10
Hg_2^{2+}	120	1820	400	30	10	30	70	15	50	30	225	1330	115	40	70	1	275	2150	100	500	2	1	2	1	10
Pb^{2+}	120	3640	400	330	500	30	70	60	1	30	110	1330	60	40	70	65	285	2150	500	875	50	100	1	50	50
Hg^{2+}	60	3640	400	1700	10	30	70	60	30	30	200	1330	115	40	70	35	280	2150	500	500	50	7.5	10	1	10
Bi^{3+}	94	1820	400	330	500	30	65	30	20	30	200	1330	60	25	70	65	1	1500	100	10	10	100	10	10	1
Cu^{2+}	60	900	10	1.2	1	30	25	15	10	30	220	130	70	25	60	65	10	2150	1	25	10	3.2	6	50	100
Cd^{2+}	120	1820	200	12	250	30	56	80	50	30	60	1330	115	25	60	65	56	12	500	1	50	100	50	50	100

forces of the paper, and this strongly limits their effect on the precipitates formed. As a result of this, the size of the precipitation zone of an individual cation on a chromatogram washed with an acid solution hardly differs at all from that of the same precipitate washed with distilled water. For this reason, the acidity of the test solution does not appear to interfere during chromatographic separation of inorganic cations by precipitation chromatography on paper.

6. The Sensitivity of Reactions Used in the Qualitative Analysis of Inorganic Cations by Precipitation Chromatography on Paper. Limiting Ratios

The procedures and techniques employed in the qualitative analysis of cations by means of precipitation chromatography have been described previously [5]. In order to determine the sensitivity of the qualitative reactions and the values of the limiting ratios, a series of 15 test tubes was prepared. In the first of them was placed a solution containing 100 mg/ml of the test element, while in the next test tube was placed a solution which was twice as dilute as that in the first test tube. This process was continued so that any one tube contained solution which was twice as dilute as that of its predecessor; in this way the concentration of each element varied from 100 mg/ml in the first tube to 0.0061 mg/ml in the 15th tube.

The sensitivity of any particular reaction was established by pipetting a drop of test solution with a micropipet – the volume of a drop being 0.025 ml – onto reagent paper, the drop being taken from the fifteenth tube to start with. The primary, washed, and developed chromatograms were prepared in turn. If no color developed, or if it was not clearly defined, then a drop of test solution from the next (stronger) test tube was taken, this procedure being repeated until a clear-cut result was obtained. Results of these tests are given in Table 1.

The values of the limiting ratios (Table 2) were determined by comparison with standard chromatograms, the latter being chromatograms of single cations obtained during determination of the reaction sensitivity.

7. Quantitative Determination of Ions by Precipitation Chromatography on Paper

The possibility of carrying out a quantitative determination of single cations on the basis of the width of the precipitation zone of the cation on a washed chromatogram has already been noted (Paragraph 3).

No success was obtained for quantitative determination of a particular ion in a complex mixture by this method. In such cases the principle of limiting dilution suggested by Shemiakin and co-workers [6-7] was used. The principle of the method of limiting dilution, which is applicable to quantitative analysis of inorganic cations by precipitation chromatography, can be stated as follows: the test solution, having been diluted to a known limit with respect to any one particular ion, ceases to give a color reaction with a developer on the reaction paper. Knowing the value of the limiting dilution C, the extent of dilution of the original solution e, and the weight of the aliquot of sample A, the percentage content (P) of the element in the test sample can be determined by means of the formula:

$$P = \frac{C \cdot e \cdot 100}{A} \tag{3}$$

The experimental results obtained showed that quantitative determination of ions by this technique, while not being very accurate (the error, in relative percentages, varied from 0.45 to 18.9), is characterized by its speed and simplicity.

It would appear that the given method could be used as an express method in quantitative analysis for the control of production, and in scientific research when no great accuracy is required, or it can be used in preliminary work.

SUMMARY

1. A qualitative and quantitative relationship has been established between the width of the precipitation zone of a single cation on a washed chromatogram, and the solubility product of the precipitate, as well as a qualitative relationship with respect to a number of other factors.

2. Results have been obtained on the sensitivity of some qualitative reactions used for the analysis of inorganic cations by means of a spot test variant of precipitation chromatography on paper; limiting ratios have also been determined.

3. Sorption precipitation series on paper treated with certain precipitants have been established.

4. A method has been suggested for the quantitative determination of an individual cation, which is based on the width of the precipitation zone for the given cation on a washed chromatogram; a method has also been suggested for the quantitative analysis of complex mixtures of inorganic cations by a drop variant of precipitation chromatography on paper, in which the principle of limiting dilution is used.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF THALLIUM

PART 1. COMPLEXOMETRIC DETERMINATION OF THALLIUM

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A fairly large number of methods have been published for the quantitative determination of thallium [1, 2]. All the same, at present there are no really specific, rapid, and reliable methods for the determination of thallium in various industrial and natural objects.

Many methods are based on precipitation reactions of univalent thallium, in particular, with various sulfur-containing reagents (thionalide, mercaptobenzothiazole, sodium diethyldithiocarbamate, etc.). A number of methods have been developed which are based on the oxidation of univalent thallium to the trivalent state, and on the reduction of trivalent thallium to the univalent state. Meanwhile, formation of complex compounds of trivalent thallium has hardly been used at all in analytical chemistry. Experiments have shown that, despite current opinion, the number of such compounds is large, but they have hardly been studied at all. The first to draw attention to this fact was Feigl [3]. Even the reaction between trivalent thallium ions and disodium ethylenediaminetetracetate (Complexon III, Trilon B) has not been studied sufficiently, and, consequently, has not found practical application.

According to the work of Flaschka [4] Tl^{3+} ions form a stable complex compound with ethylenediaminetetracetic acid; the direct method which he developed for thallium determination is based on the addition of excess magnesium complexonate to a weakly acid solution of Tl^{3+}, with subsequent titration of the Mg^{2+} ions liberated in an ammoniacal medium in the presence of Eriochrome Black T. The method is complicated to carry out and is not specific. The same is true of the complexometric determination of Tl^{3+} described by Foley and Pottie [5]: this method consists of titrating excess ethylenediaminetetracetic acid with a standard solution of $Th(NO_3)_4$ in the presence of Alizarin S at a pH of 3.5; the lower pH limit at which the complex Tl^{3+} compound is stable has not been established. Complexometric determination of univalent thallium is of no practical importance in view of its nonspecificity; a compound of univalent thallium with ethylenediaminetetracetic acid is only formed at high pH values [6].

Since existing methods for the complexometric determination of Tl^{3+} do not satisfy practical requirements, we undertook a further study of the possibilities of a complexometric determination of this element. In this connection, therefore, we first of all established the lowest pH value at which the complex compound formed between trivalent thallium and ethylenediaminetetracetic acid is stable, and then studied the possibility of carrying out a direct complexometric titration of Tl^{3+} ions at low pH values and sought for a suitable chemical indicator. The result of our work was the development of a direct, fairly selective method for the complexometric titration of Tl^{3+} in some technical materials.

EXPERIMENTAL

1. In order to prepare a solution of thallic sulfate, an accurately weighed aliquot of thallous sulfate was dissolved in water, and sulfuric acid (1:1) added until the concentration was 1-2 moles/liter; the univalent thallium was then oxidized by means of ammonium persulfate, excess of which was destroyed by boiling. The solution obtained was diluted with water in a standard flask; its concentration was checked by means of the 8-hydroxyquinolate method [7]. 1 ml of the $Tl_2(SO_4)_3$ solution contained 1.74 mg Tl.

2. A solution of $Tl(NO_3)_3$ was prepared by dissolving thallic hydroxide in 2 N HNO_3; after dilution, the solution contained about 0.5 mole/liter of free HNO_3. The solution was standardized by addition of an excess of a standard arsenite solution and then back titrating excess of the latter with iodine solution in the presence of bicarbonate. To the $Tl(NO_3)_3$ solution containing about 20 mg of Tl, and which had been neutralized with $NaHCO_3$, was added 25 ml of 0.01331 N As_2O_3 which had also been neutralized beforehand to the phenolphthalein end point with sodium bicarbonate. The solution was heated for three to five minutes until the thallic hydroxide had dissolved. On cooling, excess trivalent arsenic was titrated with 0.009949 N iodine in the presence of starch. 1 ml of this solution contained 0.784 mg of thallium.

3. A $TlNO_3$ solution was prepared by dissolving metallic thallium in nitric acid. The solution was standardized by the classical chromate method (0.896 mg/ml Tl).

4. A solution of Tl_2SO_4 was prepared by dissolving the exact weight of this salt in water. 1 ml of the solution obtained contained 1.042 mg Tl.

5. The Complexon III solution was purified and prepared by Blaedel and Knight's method [8]; methanol was used instead of ethanol. A 0.01 M solution of Complexon III was prepared by dissolving the exact amount of the preparation dried in air to constant weight; a 0.001 M solution was prepared by dilution of the 0.01 M solution.

6. A 0.1% solution of 1-(2-pyridylazo)-2-naphthol in methanol was used as the indicator for Tl^{3+} ions.

7. Buffer solutions were prepared by mixing 1 M CH_3COOH + 1 M CH_3COONa. Clark and Labs buffer solutions (0.2 N KCl + 0.2 N HCl) with pH values of 1.0, 1.2, 1.6, 1.8, and 2.0 were also used, as well as similar buffer solutions which were prepared by mixing 0.2 N K_2SO_4 and 0.2 N H_2SO_4. 1 M $CH_2Cl \cdot COOH$ and 2 N NH_4OH were used in addition, for creating the necessary pH value in the solution to be titrated.

8. Amperometric titration with a rotating platinum microelectrode (l = 4.5 mm, d = 0.5 mm) was carried out on the usual setup. The reference electrode was a saturated calomel electrode.

DISCUSSION OF RESULTS

The lower pH limit at which the complex of trivalent thallium with ethylenediaminetetracetic acid is stable, as well as the possibility of carrying out a complexometric titration of thallium at a pH of 1.0-2.0, were established by the amperometric method using a rotating platinum micro-cathode; a dropping mercury cathode was not used because of anodic dissolving of the mercury at the reduction potential of the Tl^{3+} ion [9]. Tl^{3+}, on a platinum electrode, gives a clearly defined reduction current, starting at a potential of about + 0.5 volt (Figure 1). Amperometric titration was found to be possible without applying an external emf. The equivalence point was established by the disappearance of the reduction current of Tl^{3+}. Titration was carried out without removal of dissolved atmospheric oxygen on 20-25 ml; to the solution (1-5 ml) of $Tl(NO_3)_3$ or $Tl_2(SO_4)_3$ was added NH_4OH until the pH was 1-2 according to universal indicator paper; this was followed by 15-20 ml of one of the buffer solutions mentioned above. Results of titrating Tl^{3+} in supporting electrolytes of chloride and sulfate buffer solutions showed that (Figure 2) the lowest pH value at which Tl^{3+} can be titrated in 0.2 N chloride solution is somewhat higher (pH 1.4-1.6) than in 0.2 N sulfate solution (pH 1.0-1.2). This can be explained, presumably, by formation of chloride complexes of trivalent thallium which approximate in stability to the complex of thallium with ethylenediaminetetracetic acid at pH 1.0-1.2. The strong adsorption of thallium on the strongly basic anion exchange resin Dowex 1 from hydrochloric acid solutions, and the difficulty of eluting thallium from the column [10], indicate the possibility of the formation of stable chloride complexes of trivalent thallium. Complete removal of thallium from a column is only possible by using a solution free from chloride ions (4 M $HClO_4$ or HNO_3).

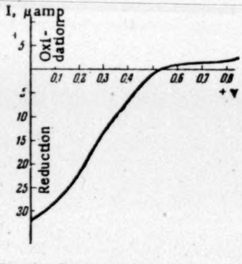

Fig. 1. Current-voltage curves for $4 \cdot 10^{-4}$ M $Tl_2(SO_4)_3$ in 1 N H_2SO_4.

Titration of Tl^{3+} with Complexon III at a pH of 1.0-2.0 in the presence of 0.2 M KBr is impossible be-

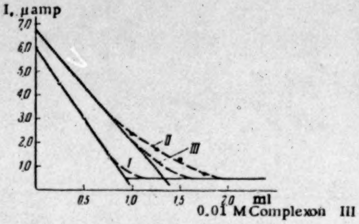

Fig. 2. Amperometric titration curves for $4 \cdot 10^{-4}$ M $Tl_2(SO_4)_3$ in 1 N H_2SO_4: I) in a supporting electrolyte of a sulfate buffer with a pH of 1.2; II) in a supporting electrolyte of a chloride buffer with a pH of 1.2; III) in a supporting electrolyte of a chloride buffer with a pH of 1.4.

cause of the higher stability of the bromide complexes of Tl^{3+} in the presence of excess Br^- ions. But on addition to a solution containing Tl^{3+} of potassium bromide in an amount corresponding to that theoretically necessary for formation of $TlBr_4^-$ ions, Br^- ions do not appreciably affect titration results, since in this case, the complex $TlBr_4^-$ dissociates to a considerable extent and is less stable than the complex with ethylenediaminetetracetic acid. Amperometric titration of Tl^{3+} with Complexon III in sulfate buffer solutions gives satisfactory results (Table 1).

Increases in the pH of the solution lead to a decrease in the reduction current of Tl^{3+} ions as a result of hydrolysis; this means an appreciable decrease in the sensitivity and accuracy of determination.

Since at present there is no suitable indicator for trivalent thallium ions, we studied an azo dye synthesized by A.E. Chichibabin [11] as an indicator; this azo dye has a pyridine ring as the first component 1-(2-pyridylazo)-2-naphthol. As Cheng and Bray [12] have shown, the azo dye gives intensely colored complexes with many cations (including Tl^+ at a pH of 10), and can be used for the complexometric determination of zinc and cadmium at pH 5-7, and of copper in an acetic acid solution. The azo dye is finding more and more applications as an indicator for the complexometric titration of a number of elements. We found that Tl^{3+} ions in nitric, sulfuric, and acetic acid solutions, at concentrations of 10^{-4} M and higher, form a red-violet complex with 1-(2-pyridylazo)-2-naphthol, starting at a pH of about 1. With decreasing Tl^{3+} concentration, the color change of the indicator from yellow to red-violet on addition of one drop of a solution of a Tl^{3+} salt, becomes clear cut at somewhat higher pH values, namely at 1.9-2.0. Chloride and bromide ions destroy the color of the complex by forming, presumably with Tl^{3+}, more stable complex compounds than the azo dye.

TABLE 1

Amperometric Determination of Thallium at pH 1.0-2.0

Thallium, in mg		Error		pH
taken	found	in mg	in %	
1.58	1.58	0	0	1.0
1.58	1.53	−0.05	−2.2	1.2
1.58	1.58	0	0	1.2
2.35	2.33	−0.02	−1.8	1.2
2.35	2.29	−0.06	−2.5	1.2
3.48	3.48	0	0	1.8
3.48	3.39	−0.09	−2.6	1.8
4.35	4.37	+0.02	+0.5	2.0
5.22	5.27	+0.05	+0.9	1.2

During titration of solutions of $Tl_2(SO_4)_3$ in the presence of 1-(2-pyridylazo)-2-naphthol with 0.01 M Complexon III, satisfactory results were obtained at a pH of 1.8-2.0 and higher (Table 2).

On the basis of the results obtained, the following indicator method has been developed for the complexometric determination of thallium.

To the solution containing Tl^{3+} ions is added 2 N NH_4OH, dropwise, until a bright yellow color develops [beginning of precipitation of $Tl(OH)_3$], an equal volume of 1 M $CH_2ClCOOH$ is then added, and the solution titrated with 0.01 M Complexon III in the presence of a few drops of indicator until the color changes from red-violet to yellow. 1 ml of 0.01 M Complexon III solution corresponds to 2.044 mg of Tl. During determin-

TABLE 2

Complexometric Titration of Trivalent Thallium in the Presence of 1-(2-Pyridylazo)-2-Naphthol

Thallium, in mg		Error		pH*	Thallium, in mg		Error		pH*
taken	found	in mg	in %		taken	found	in mg	in %	
0.69**	0.69	0	0	2.0–2.5	8.70	8.65	–0.05	–0.6	1.8
0.69**	0.68	–0.01	–1.4	2.0–2.5	8.70	8.71	+0.01	+0.1	2.0
1.38**	1.38	0	0	2.0–2.5	8.70	8.65	–0.05	–0.6	2.0
1.38**	1.37	–0.01	–0.6	2.0–2.5	8.70	8.71	+0.01	+0.1	2.1
3.48	3.45	–0.03	–0.9	1.6	8.70	8.71	+0.01	+0.1	2.1
3.48	3.46	–0.02	–0.6	4.0–4.5	8.70	8.65	–0.05	–0.6	2.6
3.48	3.50	+0.02	+0.02	4.0–4.5	8.70	8.71	+0.01	+0.1	2.8
4.35	4.28	–0.07	–1.6	1.3	8.70	8.70	0	0	3.6
4.35	4.39	+0.04	+0.9	3.5	8.70	8.70	0	0	3.8
6.96	6.90	–0.06	–0.9	1.5	8.70	8.76	+0.06	+0.7	4.0–4.5
8.70	8,59	0.11	1.3	1.2	8.70	8.65	–0.05	–0.6	4.0–4.5
8.70	8.60	–0.10	–0.9	1.4	26.11	26.06	–0.05	–0.3	4.0–4.5
8.70	8.59	–0.11	–1.2	1.7					

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*Measured with a glass electrode. Although a glass electrode does not give accurate results at such pH values, nevertheless, the approximate results obtained completely characterize the possibilities of the method.

**Titration with 0.001 M Complexon III solution.

ation of Tl^+, it is oxidized first to Tl^{3+} by means of $(NH_4)_2S_2O_8$ at a H_2SO_4 concentration of 1 mole/liter. The method also gives good results for univalent thallium (Table 3).

Complexometric determination of Tl^{3+} with an indicator at a pH of 2 is possible in the presence of large amounts of Cd, Zn, and Pb (Table 4). In such cases, trivalent thallium in the form of a standard solution was added to a known volume of the solution of the metal salt and then titration carried out as usual.

TABLE 3

Complexometric Determination of Univalent Thallium (After its Oxidation to Tl^{3+}) in the Presence of 1-(2-Pyridylazo)-2-Naphthol

Thallium, in mg		Error	Thallium, in mg		Error
taken	found	in mg	taken	found	in mg
4.48	4.49	+0.01	5.21	5.18	–0.03
4.48	4.55	+0.07	5.21	5.22	+0.01
4.48	4.45	–0.02	1.04	0.95	–0.09
8.96	8.92	–0.04	1.04	1.03	–0.01
8.96	9.08	+0.12	1.04	1.05	+0.01
8.96	8.98	+0.02	0.73	0.74	+0.01
5.21	5.20	–0.01	0.54	0.47	–0.05

Cu^{2+}, Ni^{2+}, Fe^{3+}, and Bi^{3+} interfere with the visual titration of thallium when the indicator method is used since they form colored complexes with the azo dye at a pH of about 2 [12]; Cl^-, Br^-, and I^- interfere because they destroy the color of the complex formed between Tl^{3+} and 1-(2-pyridylazo)-2-naphthol, while colored MnO_4^-, Cr_2O_7, etc. ions also interfere. Consequently, it was of interest to get a more detailed idea of the effect of other ions during amperometric titration with Complexon III solution which should be more specific. Experiments showed that Cd^{2+}, Zn^{2+}, Pb^{2+}, and Ni^{2+} ions which do not give a reduction current at E = 0 volt, and do not form stable complex compounds with Complexon III at a pH of 1.0-2.0, do not interfere with the amperometric titration of Tl^{3+} (Table 5). Fe^{3+}, Bi^{3+}, Cu^{2+} which form complexes at pH 1.0-2.0 interfere with the amperometric determination of Tl^{3+} and should be removed beforehand. In the same way, ions of oxidizing agents which give reduction currents at E = 0 volt (MnO_4^-, $Cr_2O_7^{2-}$, $S_2O_8^{2-}$, etc.) interfere. Despite this, amperometric titration of Tl^{3+} possesses a number of advantages over visual titration, since it permits determina-

TABLE 4

Determination of Thallium in the Presence of Other Cations

Taken, in mg				Ratio	Found	Error
Tl	Cd	Zn	Pb	Tl : Me	Tl, in mg	in mg
8.70	86	–	–	1 : 10	8.67	−0.03
3.48	86	–	–	1 : 25	3.45	−0.03
3.48	258	–	–	1 : 70	3.50	+0.02
1.74	435	–	–	1 : 250	1.75	+0.01
1.74	435	–	–	1 : 250	1.75	+0.01
3.48	2340	–	–	1 : 675	3.40	−0.08
3.48	2340	–	–	1 : 675	3.60	+0.12
3.48	2340	–	–	1 : 675	3.50	+0.02
3.48	–	227	–	1 : 60	3.40	−0.08
3.48	–	227	–	1 : 60	3.50	+0.02
1.74	–	454	–	1 : 250	1.79	+0.05
1.74	–	454	–	1 : 250	1.75	+0.01
1.57	–	681	–	1 : 400	1.56	−0.01
1.57	–	908	–	1 : 600	1.61	+0.04
1.57	–	1135	–	1 : 700	1.69	+0.12
6.96	–	–	1075	1 : 150	6.90	−0.06
6.96	–	–	1075	1 : 150	6.90	−0.06
3.48	–	–	1075	1 : 300	3.54	+0.06
3.48	–	–	2150	1 : 600	3.68	+0.20
3.48	–	–	2150	1 : 600	3.60	+0.12

TABLE 5

Amperometric Titration of Tl^{3+} in the Presence of Cd, Zn, Pb, and Ni

Added, in mg				Thallium, in mg		Error, in mg
Cd	Zn	Pb	Ni	taken	found	
258	100	100	50	2.35	2.37	+0.02
258	200	250	25	1.57	1.53	−0.04
344	200	250	100	2.35	2.35	0

tion in the presence of Cl^- ions at pH 1.4-2.0 and, furthermore, permits determinations to be carried out in turbid and colored solutions.

Determination of thallium in briquet cadmium. An aliquot of cadmium (1.0-1.5 g) is dissolved on heating in 10 ml of 2 N H_2SO_4 and 1-2 ml of concentrated HNO_3. The solution is heated on a sand bath to remove nitrogen oxides, about 0.1 g of $(NH_4)_2S_2O_8$ is then added (if a raspberry color appears because of the presence of MnO_4^-, 5 ml of 5% HCl is added; the MnO_2 formed does not cause any further trouble). The solution is next heated to remove excess $(NH_4)_2S_2O_8$ and neutralized with 2 N NH_4OH to a pH of about 2.0 using universal indicator paper; it is finally titrated amperometrically with 0.01 M Complexon III.

Determination of thallium in slag. An aliquot of test material is dissolved in 10-20 ml of 0.5 N HNO_3 and the univalent thallium oxidized by means of $(NH_4)_2S_2O_8$; the trivalent thallium is then titrated amperometrically with 0.01 M Complexon III solution at a pH of about 2.

In both cases, in order to check on the correctness of the results obtained (Table 6), a known amount of trivalent thallium was added to the solution after titration with Complexon III, and titration continued. In this way it was shown that the method gives satisfactory results for the determination of thallium in the materials indicated.

TABLE 6

Determination of Thallium in Technical Products

Test sample	Weight, in g	Tl found, in %	Tl added, in %	Amount of Tl that should be present, in %	Amount actually found, in %	Error, in %
Briquet cadmium (containing 0.15% Tl according to factory analysis)	1.2635	0.19	0.31	0.50	0.54	+0.04
	1.1686	0.16	0.46	0.62	0.59	−0.03
	1.3402	0.18	0.18	0.36	0.36	0
	1.3402	0.18	0.30	0.48	0.47	−0.01
Slag	0.1503	1.30	1.56	2.86	2.88	+0.02
	0.2181	1.24	–	–	–	–
	0.2204	1.31	1.07	2.38	2.46	+0.08
	0.2067	1.17	1.51	2.68	2.66	−0.02

SUMMARY

1. It has been shown that it is possible to carry out an amperometric titration of trivalent thallium with Complexon III at pH ≥ 1.2 (in the absence of large amounts of Cl^- and Br^- ions), and at pH ≥ 1.4 (in the presence of appreciable amounts of Cl^-).

2. 1-(2-Pyridylazo)-2-naphthol serves as an indicator for Tl^{3+} and permits visual titration of Tl^{3+} with Complexon III at a pH of about 2 and higher.

3. Large amounts of Zn, Cd, and Pb do not interfere with the complexometric determination of thallium. The method is suitable for the analysis of technical materials.

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THE USE OF COMPLEXONS IN POLAROGRAPHY

PART 2. THE BEHAVIOR OF MOLYBDENUM ON THE DROPPING MERCURY ELECTRODE IN A SUPPORTING ELECTROLYTE OF COMPLEXONS*

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The polarographic behavior of molybdate ions in acid solutions has been studied several times [1-6]. All the same, the mechanisms of the electrode reactions which occur cannot be regarded as established because of the complexity of the chemistry of sexivalent molybdenum; this is particularly true, since hitherto there has been no agreement between the data given for the nature of the molybdenum ions at various pH values. Many workers consider that the molybdate ion (MoO_4^{2-}) only exists at a pH of 7 and higher; on increasing the acidity, the ions $Mo_3O_{11}^{4-}$, $Mo_6O_{21}^{6-}$, $Mo_{12}O_{41}^{10-}$, and $Mo_{24}O_{78}^{12-}$ are formed, while at a pH of about 1, molybdenum may even be found in solution as the cation [7].

Some work has been carried out on the behavior of molybdate ions on a dropping mercury electrode in the presence of complexing agents. For example, Uhl [8] reduced molybdate in dilute solutions of nitric acid containing lactic and oxalic acids, and obtained two waves. The half-wave potential of the first was $E_{1/2} = -0.35$ volt, while that of the second was $E_{1/2} = -0.5$ volt (relative to the saturated calomel electrode). Nevertheless, as Johnson and Robinson [5] have pointed out, in the presence of nitrate ions there is obtained a catalytic wave for NO_3^- at the potential corresponding to the reduction of Mo^V to Mo^{III}, a fact which Uhl did not take into account;he was thus led to wrong conclusions. Good waves have been obtained for phosphomolybdic and silicomolybdic acids [9]. Recently, for analytical purposes, we suggested a method for determining micro amounts of molybdenum on the basis of the catalytic wave obtained in $HClO_4$ solutions [10]. Complexon III permits polarographic determination of molybdenum in the presence of tungsten and a number of other cations [11].

Results are given in the present article of a study of the behavior of the complexes formed between molybdenum and Complexon I (nitrilotriacetic acid) and Complexon III (disodium ethylenediaminetetracetate) respectively, on a dropping mercury electrode, as well as of a study of the behavior of the complexes formed between molybdenum and some new complexons; the effect of various factors were studied (pH, complexon concentration, height of the mercury column, etc.).

The work was carried out on a recording polarograph with a galvanometer whose sensitivity was $3.33 \cdot 10^{-9}$ µamp/mm/m. The capillary characteristics were $m = 1.98$ mg·sec^{-1}; $t = 4.2$ sec; $t^{1/6} = 2.00$ mg$^{2/3}$·sec$^{-1/2}$. The electrolyzer was provided with a sleeve through which water from a thermostat operating at 25 ± 0.1° was circulated. The anode was a saturated calomel electrode which was connected to the electrolyzer through an agar-agar bridge, prepared from a semi-saturated solution of potassium chloride. The values quoted throughout for the potentials are relative to the saturated calomel electrode. The pH was measured by means of an AP-4 tube potentiometer.

Ammonium molybdate solution was prepared by dissolving MoO_3 in a small excess of ammonia, the solution was then boiled until the odor of ammonia was no longer observable, and was finally diluted with water to the requisite volume. The molybdenum content was determined gravimetrically as lead molybdate.

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*Part 1, see J. Anal. Chem. 8, 333 (1953) (see C.B. translation).

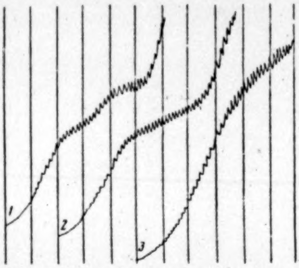

Fig. 1. Polarograms for ammonium molybdate ($1.04 \cdot 10^{-3}$ M) in a supporting electrolyte of acetic acid: 1) 5 M CH_3COOH; 2) 10 M CH_3COOH; 3) 15 M CH_3COOH.

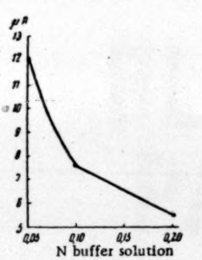

Fig. 2. Relation between the value of the diffusion current for molybdate ions and the concentration of the buffer solution of 0.1 N acetic acid and 0.1 N ammonium acetate, pH 4.6.

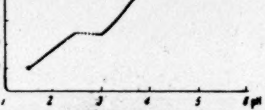

Fig. 3. Relation between the value of $E_{1/2}$ for molybdenum in the presence of Complexon I and pH: Mo concentration = $= 1.04 \cdot 10^{-3}$ M; Complexon I concentration = 0.05 N (in 0.1 N acetate buffer).

Solutions of lead, cadmium, and tungsten salts, as well as solutions of the other necessary materials, were prepared by dissolving the chemically pure preparations or analytical grade recrystallized salts.

The buffer solution with a pH of 4.6 consisted of equal volumes of 0.1 N acetic acid and 0.1 N ammonium acetate.

All the complexons were dissolved in the buffer solution. Complexons I and III were dissolved after recrystallization from a mixture of methanol and acetone (2:1).

On Figure 1 are shown the polarograms for molybdate ($1.04 \cdot 10^{-3}$ M) in 5, 10, and 15 M acetic acid. In 5 M acetic acid, molybdate gives two waves with $E_{1/2} = -0.27$ volt, and $E_{1/2} = -0.73$ volt. On increasing the acetic acid concentration, only one extended wave with a half-wave potential displaced to more negative values is obtained. In the buffer solution of 0.1 N acetic acid and 0.1 N ammonium acetate, with a pH of 4.6, the half-wave potential of molybdate is equal to -0.66 volt, and does not change with the changes in concentration of the buffer solution in the limits of 0.05-0.2 M. The value of the diffusion current decreases with increasing concentration of the buffer solution (Figure 2).

Complexon I. Molybdenum, in the presence of Complexon I gives a clearly-defined reduction wave in acid solutions; its half-wave potential depends on the pH. On Figure 3 is shown the relationship between $E_{1/2}$ and pH in a 0.1 N solution of acetate buffer and 0.05 M Complexon I.

As is evident from Figure 3, on increasing the pH from 1.5 to 4.5, the half-wave potential for molybdate shifts to more negative values. In the range pH 2.5-3, the wave breaks up into three waves and, on increasing the pH further, one wave is again obtained, the half-wave potential of which increases on the negative side; it reaches a maximum at 4.5 and then starts to shift gradually toward positive potentials. In alkaline solutions (pH 8-10) the wave disappears, indicating thereby the instability of the complex in alkaline solutions.

The optimum condition for obtaining a molybdenum wave is a pH of 4.5-5.5. At pH 1.5, there is obtained one wave whose height is only half of that obtained at pH 4.5-5.5 (Figure 4). All these facts indicate that reduction of molybdenum in the presence of Complexon I is a complicated one, in which there are intermediate stages at various pH values. Since the value of the diffusion current for molybdenum in the presence of Complexon I depends so strongly on the pH of the solution, a technique based on this Complexon is not expedient for quantitative determination of molybdenum.

Complexon III. Molybdate ions form a compound with Complexon III since, on addition of the latter to a molybdate solution, the half-wave potential shifts to more negative values (the pH of the solution was the same in both solutions). The nature of the polarogram obtained for molybdenum in the presence of Complexon III depends strongly on

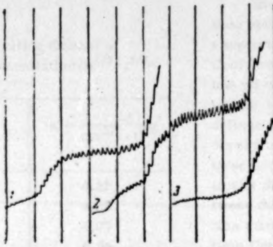

Fig. 4. Polarograms for $1.04 \cdot 10^{-3}$ M molybdate in 0.1 N buffer solution – 0.05 Complexon I solution, at various pH values: 1) pH 1.5; 2) pH 2.5; 3) pH 5.5

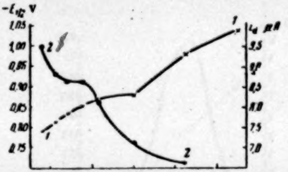

Fig. 5. Relation between the values of $E_{1/2}$ (Curve 1) and i_d (Curve 2) of molybdenum, and the concentration of Complexon III.

the pH, on Complexon III concentration, and on other factors.

In order to establish the influence of Complexon III concentration, various amounts of the latter were added to a $1.04 \cdot 10^{-3}$ M solution of molybdate in 0.1 N buffer solution. At Complexon III concentrations greater than 0.1 M, diffuse, extended waves are obtained; at concentrations below 0.1 M, clearly defined waves are obtained whose height is determined to some extent by the concentration. The half-wave potential shifts to more negative values with increasing Complexon III concentration. On Figure 5 is shown the relation between $E_{1/2}$ (Curve 1) and i_d (Curve 2) of molybdenum and Complexon III concentration. As can be seen from Figure 5, on the part of Curve 1 corresponding to Complexon III concentrations ranging from 0.06 to 0.1 M, the half-wave potential maintains a constant value of −0.87 volt; since the wave of the complex is most clearly defined at a Complexon III concentration of 0.065 M, further work was carried out at this concentration.

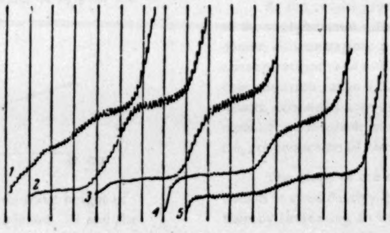

Fig. 6. Polarograms for $1.04 \cdot 10^{-3}$ M molybdate in 0.1 N acetate buffer – 0.065 M Complexon III at various pH values: 1) pH 2.45; 2) pH 4.22; 3) pH 6.70; 4) pH 7.51; 5) pH 8.32.

TABLE 1

Relation Between the Limiting Current of Molybdenum and its Concentration ($m^{2/3} \cdot t^{1/6} = 2.00$ mg$^{2/3} \cdot$ sec$^{-1/2}$)

Mo concentration, in mmole/liter	i_d μa, obtained	$K = \frac{i_d}{cm^{2/3} \cdot t^{1/6}}$
1.042	9.091	4.35
0.521	4.695	4.50
0.261	2.597	4.97
0.208	2.098	5.04
0.156	1.798	5.76
0.104	1.199	5.78
0.052	6.616	5.91
0.021	0.250	5.95

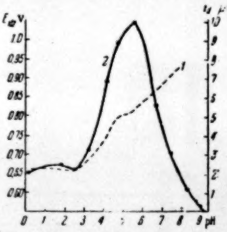

Fig. 7. Relation between the value of $E_{1/2}$ (Curve 1) and i_d (Curve 2) of molybdenum, and pH, in a supporting electrolyte of Complexon III (at pH< 4, values of $E_{1/2}$ for the second wave are given).

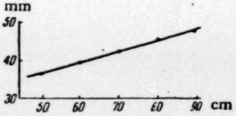

Fig. 8. Relation between wave height of molybdenum with Complexon III and the height of the mercury column (h).

In order to clarify the effect of pH, polarograms were obtained for a $1.04 \cdot 10^{-3}$ M solution of molybdate in a supporting electrolyte of 0.1 N acetate buffer – 0.065 M Complexon III at various pH values. It was found that at low pH values, there is obtained two step-like, extended waves; in the pH range 4-7, there is obtained one clearly-defined wave, whose half-wave potential and wave height depend to a lesser extent on pH. In alkaline solutions, the wave decreases sharply and, at a pH greater than 8, practically disappears completely (Figure 6). The relation between the half-wave potential and the value of the diffusion current, and pH is shown on Figure 7. As can be seen from Curve 1, the value of $E_{1/2}$ is constant in the limits pH 0-2.5; beyond this range, with increasing pH, the values of the half-wave potential shift strongly to negative values. The diffusion current increases with increasing pH (from pH 2.5), passes through a maximum at pH 5.5, drops again with increasing pH, and approximates to zero at pH about 9. Further work was accordingly carried out at this pH of 5.5.

In order to establish the nature of the limiting current obtained, polarograms were taken for $5.20 \cdot 10^{-4}$ M molybdate in a supporting electrolyte of 0.1 N buffer – 0.065 M Complexon III (pH 5.5), at various values of the height of the mercury column. As can be seen from Figure 8, the value of the limiting current of molybdenum depends on the height of the mercury column; accordingly, the limiting current is determined by diffusion.

The relation between the value of the limiting current and molybdenum concentration was investigated by taking polarograms of solutions containing different concentrations of molybdenum on a supporting electrolyte of 0.1 N acetate buffer – 0.065 M Complexon III with a pH of 5.5. The results obtained are given in Table 1.

As the results given in this table show, the constant of the molybdenum diffusion current changes with molybdenum concentration; it increases at lower molybdenum concentrations and remains practically constant in the concentration range 0.156-0.21 mmole/liter. For molybdenum concentrations up to $1.5 \cdot 10^{-4}$ M, the value of the constant corresponds to a process involving three electrons, i.e., to reduction of Mo^{VI} to Mo^{III}.

The slope of the current-voltage curve for molybdenum is considerably greater than the theoretical value, thereby indicating an irreversible character for the reduction process. Actually, on constructing a curve for $E - \log \frac{i}{i_d - i}$, a value of 6 was found for n, which should lead one to assume that reduction of Mo^{VI} to metal occurs. Such an assumption, of course, has no foundation in fact and consequently the process must be regarded as irreversible. In order to determine the number or electrons participating in the electrode reaction, a microcoulometric method proposed by Stromberg and Markacheva [12] was also used.

Numerous coulometric experiments also gave a value for n of about 5-6.

TABLE 2

Effect of Fe, Cu, Pb, Zn, V and W on the Values of the Limiting Current of Molybdenum in Complexon III as Supporting Electrolyte

Mo conc. in μg/ml	Concentration of added impurities, in μg/ml						Found i_d μa
	Fe	Cu	Pb	Zn	W	V	
5	—	—	—	—	—	—	0.45
5	5	—	—	—	—	—	0.46
5	25	—	—	—	—	—	0.45
5	50	—	—	—	—	—	0.38
100	—	—	—	—	—	—	9.01
100	100	—	—	—	—	—	7.49
100	500	—	—	—	—	—	6.16
100	1000	—	—	—	—	—	Not determined
5	—	5	—	—	—	—	0.45
10	—	—	—	—	—	—	0.90
10	—	50	—	—	—	—	0.80
100	—	100	—	—	—	—	6.83
100	—	500	—	—	—	—	5.99
5	—	—	5	—	—	—	0.47
5	—	—	25	—	—	—	0.47
5	—	—	50	—	—	—	0.63
5	—	—	—	50	—	—	0.46
5	—	—	—	—	50	—	0.46
100	—	—	—	—	—	100	8.83
100	—	—	—	—	—	1000	9 32

TABLE 3

Relation Between the Values of $E_{1/2}$ and i_d of Molybdenum in the Presence of Disodium Benzhydrylaminediacetate, and pH

Mo concentration, $M \cdot 10^{-4}$	pH	$-E'_{1/2}$ v	$-E''_{1/2}$ v	i'_d μa	i''_d μa
2.6	1.5	0.10	0.33	1.00	0.90
2.6	2.7	0.22	0.44	0.33	1.00
2.6	4.5	0.25	0.54	0.26	0.56
2.6	6.5	0.15	1.11	0.67	1.0
2.6	8.5-10.0	No wave		—	—

The influence of Fe^{III}, Cu, Pb, Zn, W, and V on the reduction wave of molybdenum in a solution of 0.1 N acetate buffer − 0.065 M Complexon III was also studied. The results obtained are given in Table 2.

It follows from Table 2 that iron, copper, and lead, when present in amounts which are ten times that of molybdenum, affect the polarographic determination of molybdenum in the presence of Complexon III. Tungsten, in amounts which are ten times those of molybdenum does not affect the height of the molybdenum wave. Vanadium only interferes at high concentrations of this element. Thus, by separating molybdenum from iron and copper, it can be determined in the presence of lead, zinc, and tungsten; this confirms the results obtained by Pribil and Blazek [11].

Other Complexons. Reduction of molybdenum in the presence of disodium benzhydrylamineacetate and disodium hexamethylenediaminetetracetate, synthesized by Lastovskii and co-workers [3], was also studied, as well as its reduction in the presence of cyclohexanediaminetetracetic acid.*

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*Synthesized by M.N. Shchunkina in the Ordzhonikidze All-Union Scientific Research Chemical Pharmaceutical Institute.

TABLE 4

Relation Between the Values of $E_{1/2}$ and i_d for Molybdenum in the Presence of Hexamethylenediaminetetracetic Acid, and pH

Mo concentration, $M \cdot 10^{-4}$	pH	$-E_{1/2}$ v	i'_d μa
2.6	1.5	0.31	2.75
2.6	2.5	0.37	3.20
2.6	3.5	0.56	3.16
2.6	4.5	0.55	1.76
2.6	6.0-10	No wave	

TABLE 5

Relation Between the Values of $E_{1/2}$ and i_d for Molybdenum in the Presence of Cyclohexanediaminetetracetic acid, and pH (Mo concentration = $5.2 \cdot 10^{-4}$ M; Complexon concentration 0.05 M)

pH	$-E_{1/2}$ v	i_d μa
1.5	No wave	–
2.5	0.42	2.17
4.0	0.47	2.25
5.0	0.63	3.20
6.0	0.70	0.66
7.5-9.5	No wave	

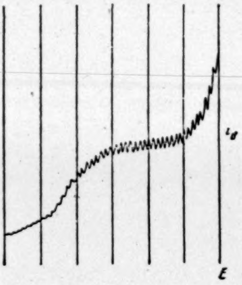

Fig. 9. Polarogram for molybdate in a supporting electrolyte of 0.1 N acetate buffer – 0.04 M hexamethylenediaminetetracetic acid – pH 2.5

Molybdenum in the presence of disodium benzhydrylaminediacetate gives very poorly defined, small waves in acid and neutral solutions only. The half-wave potential and the value of the diffusion current depend to a very large extent on the pH of the solution (Table 3).

On comparing Table 3 with Figure 7 it is clear that the diffusion current of molybdenum in the presence of Complexon III is several times greater than with the test complexon and, consequently, the latter has no advantages over Complexon III.

Molybdenum in the presence of hexamethylenediaminetetracetic acid gives one or two clearly defined waves in a 0.1 N acetate buffer, which is 0.05 M with respect to the complexon, according to the pH value. Table 4 contains results for the half-wave potentials and diffusion current of molybdenum as functions of the pH.

It should be noted that in acid solutions at all pH values, the molybdenum wave consists of two parts which are not clearly defined (Figure 9). Accordingly, the values of $E_{1/2}$ given in Table 4 are arbitrary values, since they are calculated on the basis of the whole wave.

It is, however, quite obvious from Table 4 that with increasing pH, the half-wave potential of molybdenum shifts to more negative values, while the diffusion current decreases, starting at pH 4.5. In solutions with pH 6, an extended curve is obtained which is difficult to measure, while at pH 8-10 there is no wave at all. On comparing the results obtained with those obtained for Complexon III, it is clear that hexamethylenediaminetetracetic acid has no advantages over Complexon III for the polarographic determination of molybdenum.

In the presence of cyclohexanediaminetetracetic acid, molybdenum, in a supporting electrolyte of 0.1 acetate buffer, is reduced on a dropping mercury cathode to give a clearly defined wave in acid solutions only, over a narrow pH range. The half-wave potential is dependent on pH (Table 5); in neutral and alkaline solutions no wave appears at all.

In strongly acid solutions (pH 1.5), no molybdenum wave is obtained, the complexon is precipitated under these conditions. With increasing pH the half-wave potential shifts to more negative values, while the diffusion current achieves a maximum value at pH 5. It follows from this that the optimum condition for reducing molybdenum is a buffer solution with a pH of 5. Nevertheless, on comparing the value of the diffusion current of molybdenum with this complexon, with that obtained with Complexon III, it is evident that it has no advantages over the latter.

SUMMARY

A study has been made of the reduction of molybdenum on a dropping mercury electrode in the presence of Complexon I, Complexon III, benzhydrylaminediacetic acid, hexamethylenediaminetetracetic acid, and cyclohexanediaminetetracetic acid.

It has been found that in all cases molybdenum is reduced in acid solutions. The half-wave potentials and the values of the diffusion currents are all strongly dependent on the pH value. No reduction waves of molybdenum are formed in alkaline solutions. It has been shown that Complexon III gives the best results from an analytical point of view.

Fe^{3+} and Cu^{2+} decrease the limiting current of molybdenum in the presence of Complexon III, while Pb, Zn, V, and W ions have practically no effect on the limiting current.

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THE SOLUBILITY OF COPPER AND SILVER REINECKE ACID SALTS

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Ammonium tetrathiocyanatoaminochromiate (Reinecke's salt) is widely used in analytical chemistry for the detection and determination of a number of metals, for example, for the spot and fractional detection of copper [1], and also for its gravimetric and titrimetric determination [2, 3], for the quantitative determination of mercury [4, 5], cadmium [4, 7], and thallium [6].

Despite the fact that Reinecke's salt has been known for a long time as an analytical reagent for the isolation from solution of copper, mercury, thallium, silver, and other metals, hitherto there has been no published data available on the solubility of the Reineckates of these metals.* In the meantime, a knowledge of the values of the solubility products of these compounds would enable analysts to be in a better position to solve questions related to the development of methods for detecting and determining a number of metals. The object of the work described in the present article was the determination of the solubilities of the Reineckates of copper and silver.

Reagents and Materials

Reinecke salt containing radioactive chromium-51 (a γ-radiator with a half-life period of 26.5 days), as well as Reinecke salt containing nonradioactive chromium were used in the present investigation.

The Reineckate of univalent copper containing radioactive chromium-51, and silver Reineckate containing the radioactive isotope of this element (a β-emitter with a half-life period of 225 days) were prepared.

Synthesis of Reinecke's salt. The Reinecke salt was prepared by the method described by Kul'berg [10]. For synthesizing Reinecke salt containing radioactive chromium, the nitrate and sulfate, and also the trioxide of chromium were used. The nitrate or sulfate of radioactive chromium were converted beforehand into ammonium dichromate by boiling with an ammoniacal solution of hydrogen peroxide.

Synthesis of copper Reineckate. To 200 ml of a 1 N solution of $CuCl_2$ acidified with 5-10 ml of concentrated HCl, and heated to the boiling point, was added a few small portions, 0.2 g each, of hydrazine hydrochloride until the solution was completely colorless. To the reduced solution at a temperature of 70° was added dropwise a saturated solution of Reinecke's salt acidified with hydrochloric acid, until formation of a precipitate ceased and a stable red color was obtained. This solution was then cooled by continuous agitation. The precipitate was filtered through a No. 4 filter and washed on the filter, first with 5% hydrochloric acid, and then with hot distilled water. Finally, the precipitate was washed with alcohol, and then with ether, and dried in a desiccator over sulfuric acid.

Synthesis of silver Reineckate. Active metallic silver-110 was dissolved on heating in nitric acid; to this solution was added an inactive solution of silver nitrate. This mixture was carefully evaporated to dryness and then dissolved in distilled water to give a 0.2 N solution. To a freshly prepared 0.08% N solution of Reinecke's salt (free from active chromium) was added a small excess of the solution of $AgNO_3$ described above. A large excess of $AgNO_3$ should be avoided, otherwise a flocculent precipitate which is difficult to filter will be formed.

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*After the present article had been sent to the J. Anal. Chem., we became aware of the article by Bagbanly on the solubilities of these salts [13].

The precipitate of $Ag[Cr(NH_3)_2(SCN)_4]$ obtained was filtered off and washed in a centrifuge until the washings no longer gave a reaction for NO_3^- ions (test with diphenylamine). It was then dried in a desiccator over sulfuric acid and analyzed.

Determination of the Solubility of Copper Reineckate

During the study of the solubility of copper Reineckate we bore in mind the fact that at infinite dilution, normal concentration and active concentration become equal [11]. The low solubility of copper Reineckate enables one to use the Nernst equation for calculating the solubility product.

The method used for determining the solubility was as follows. A sample of test material (0.05-0.12 g) was placed in the vessel to be used for the solubility determinations; this vessel was provided with stirrers, and kept in a thermostat. Distilled water or 0.01 N hydrochloric acid was then added. Saturation was reached after 10-12 hours. Samples were withdrawn by means of a pipet fitted with a filter disc made from Schott No. 1 or by filtration through a fine filter paper.

Copper was deposited from the filtrate by means of cadmium sulfide. The copper sulfide precipitate plus filter were washed, and converted first into the cupric oxide, and then into the sulfate. Copper was determined iodometrically in the sulfate by titration with 0.02 N sodium thiosulfate, using a microburet.

TABLE 1

Solubility and Solubility Product of Copper Reineckate at 15°

Solubility of the salt, in mole/liter			Solubility product in aqueous solution
in pure water		in 0.01 N HCl	
	$5.98 \cdot 10^{-5}$	$6.65 \cdot 10^{-5}$	$3.58 \cdot 10^{-9}$
	$6.20 \cdot 10^{-5}$	$6.40 \cdot 10^{-5}$	$3.84 \cdot 10^{-9}$
	$6.00 \cdot 10^{-5}$	$7.31 \cdot 10^{-5}$	$3.60 \cdot 10^{-9}$
Mean	$6.6 \cdot 10^{-5}$	$6.78 \cdot 10^{-5}$	$3.67 \cdot 10^{-9}$

Results for the determination of the solubility of copper Reineckate in water and in 0.01 N HCl at 15° are given in Table 1. The same table also contains the results for the solubility product.

The solubility of copper Reineckate in pure water ($6.6 \cdot 10^{-5}$ mole/liter) differs very little from the solubility of this salt in 0.01 N hydrochloric acid ($6.78 \cdot 10^{-5}$ mole/liter). This fact justifies the technique used for determination of small amounts of copper by precipitation of it as the Reineckate from weak hydrochloric acid solutions.

The results given in Table 1 are in good agreement with the results obtained by the radiochemical method.

Determination of the Solubilities of the Reineckates of Copper and Silver by the Method of Labelled Atoms*

The method used for the determination of sparingly soluble salts has been described several times in the literature.

500 mg of $Cu[Cr(NH_3)_2(SCN)_4]$ labelled with chromium-51 or $Ag[Cr(NH_3)_2(SCN)_4]$ labelled with silver-110, was placed in the vessel used for determination of the solubility, and 500 ml of distilled water added; the mixture was then held in a thermostat at 15°.

Saturation was reached after continuous stirring for 8-10 hours in the case of copper Reineckate and 30-32 hours in the case of silver Reineckate.

50 ml of the solution was taken by means of a pipet with a filter plug (made from Schott No. 4 filter) and transferred to a Petrie dish. The weight of solution was determined; it was then evaporated to dryness under an infra-red lamp.

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*E.A. Popovkina and V.V. Pushkarev participated in this work.

In order to prepare a standard, 0.1 g of copper Reineckate was dissolved in 50 ml of 10% HCl containing a small amount of concentrated HNO_3. The standard silver Reineckate was prepared in the same way but, in this case, nitric acid was used as the solvent. The standard solutions were also evaporated in the same way in Petrie dishes of the same size. A Type B counter with a torsion counter was used for determining the activity. During determination of the specific activity, the error resulting from insufficient evenness ofthe layer of deposit on the bottom of the Petrie dish was eliminated by rotating the dish through 360° at 90° intervals.

The activity of the sample taken for determination of the solubility was determined in the same way; it amounted to, on an average, about 300 impulses/minute in the case of copper Reineckate, and to 450 impulses/ /minute for silver Reineckate. The background intensity did not exceed 40-45 impulses/minute.

The results obtained are given in Table 2.

TABLE 2

Solubility of Copper and Silver Reineckates at 15°

Formula of test material	Solubility, in mole/liter	Indicator
$Cu[Cr(NH_3)_2(SCN)_4]$	$4.75 \cdot 10^{-5}$	Chromium-51
$Ag[Cr(NH_3)_2(SCN)_4]$	$1.71 \cdot 10^{-7}$	Silver-110

The results obtained for the solubility of copper Reineckate by means of the radioactive indicator method are very similar to those obtained by the method described above (Table 1).

A study of the composition of the bottom phases for their copper content by chemical analysis showed that they had not changed as the result of the action of water.

In conclusion, we should like to thank E.I. Krylov for his valuable advice.

SUMMARY

The solubility of copper and silver Reineckates in water at 15° has been studied. It has been found that the solubility of these salts decreases with increasing atomic weight of the test element. The solubility product of copper Reineckate at 15° has been calculated.

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DETERMINATION OF SMALL AMOUNTS OF INDIUM BY A TITRIMETRIC AND PHOTOMETRIC METHOD

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One of the few methods which have been published hitherto for the titrimetric determination of indium is based on potentiometric titration of indium by means of potassium ferrocyanide [1]. The compound formed has been ascribed the formula $KIn_3[Fe(CN)_6]_4$. Kolthoff [2] in describing this method notes, however, that "the composition of the precipitate which is formed has not yet been studied." During studies of systems including indium chloride and the ferrocyanides of lithium, sodium, potassium, rubidium, and cesium [3, 4], it was found that in their capacity to form sparingly soluble mixed ferrocyanides with indium, the alkali metals can be arranged in the following ascending order: Li < Na < K < Rb < Cs (Table 1).

TABLE 1

The Mixed Ferrocyanides of Indium and the Alkali Metals

Ferrocyanides of the alkali metals	$Li_4[Fe(CN)_6]$ $Na_4[Fe(CN)_6]$	$K_4[Fe(CN)_6]$	$Rb_4[Fe(CN)_6]$	$Cs_4[Fe(CN)_6]$
Composition of the solid phases formed in the systems: $InCl_3-Me_4[Fe(CN)_6]-H_2O$	$In_4[Fe(CN)_6]_3$	1) $In_4[Fe(CN)_6]_3$ 2) $KIn[Fe(CN)_6]$	1) Phase of variable composition: $In_4[Fe(CN)_6]_3 \times$ $\times\ Rb_4[Fe(CN)_6]$ $(x < 1)$ 2) $RbIn[Fe(CN)_6]$	1) $CsIn[Fe(CN)_6]$ 2) Phase of variable composition: $CsIn[Fe(CN)_6] \times$ $\times\ xCs_4[Fe(CN)_6]$ $(x < 1/4)$ 3) $Cs_7In_3[Fe(CN)_6]_4$

The work carried out, despite the complexity of the reactions which occur, allowed conclusions to be drawn which could be useful from an analytical point of view.

In the light of the results which we obtained, it is completely obvious that the reason for the inaccuracy of the potentiometric method indicated above; is the variable composition of the precipitate formed thus, for a ratio of $K_4[Fe(CN)_6] : InCl_3 = 0.75$ in the original mixture, the normal ferrocyanide of indium is formed, which then reacts with $K_4[Fe(CN)_6]$ to form a mixed salt $KIn[Fe(CN)_6]$, as a result of which the potential change observed is not clearly defined.

The only compound which has a definite composition is formed when indium ions react with lithium and sodium ferrocyanides. The equivalence point during potentiometric titration is observed, in this case, at ratios of the components corresponding to the formation of $In_4[Fe(CN)_6]_3$.

From what has been said above, it follows that for the analytical determination of indium, the ferrocyanides of lithium and sodium should have preference over those of potassium, rubidium, and cesium. Accordingly, in our subsequent work on the titrimetric determination of indium, we used sodium ferrocyanide as being the most readily available and cheapest reagent.

Titrimetric Determination of Indium

A high resistance potentiometer type PPTV 1 was used for potentiometric titration in conjunction with a galvanometer with a shadow scale. A saturated calomel electrode was used as the standard half-element. The indicator electrode was a platinum one. The salt bridge was a saturated KCl solution.

TABLE 2

Potentiometric Titration of $InCl_3$ by Means of $Na_4[Fe(CN)_6]$

$InCl_3$, 40 ml 0,00547 *M*			$InCl_3$, 40 ml 0,01 *M*		
$Na_4[Fe(CN)_6]$ 0.0328 *M*	emf, in mv	$\frac{Na_4[Fe(CN)_6]}{InCl_3}$	$Na_4[Fe(CN)_6]$ 0,0328	emf, in mv	$\frac{Na_4[Fe(CN)_6]}{InCl_3}$
0.2	0.333	0.03	2.0	0.387	0.16
			4.0	0.399	0.33
1.0	0.387	0.15	6.0	0.420	0.49
			7.0	0.450	0.57
1.6	0.416	0.24	7.4	0.480	0.61
2.0	0.456	0.30	7.8	0.500	0.64
			8.2	0.500	0.67
3.0	0.479	0.45	8.9	0.550	0.73
3.8	0.489	0.57	9.0	0.550	0.74
4.0	0.489	0.60	9.05	0.570	0.74
4.4	0.489	0.66	9.10	0.590	0.74
4.8	0.537	0.72	9.15	0.615	0.75
5.0	0.537	0.75	9.20	0.350	0.75
5.2	0.270	0.78	9.25	0.300	0.76
5.4	0.200	0.81	9.30	0.252	0.76
6,0	0.135	0.90	9.50	0.201	0.78

TABLE 3

Titration of Indium With a Solution of $Na_4[Fe(CN)_6]$

In^{3+} taken, in g	In^{3+} found, in g
0.0010	0.0010
0.0017	0.0016
0.0026	0.0026
0.0034	0.0035
0.0050	0.0050
0.0068	0.0067
0.0085	0.0087
0.0100	0.0103
0.0200	0.0190
0.0400	0.0400
0.1000	0.0990

TABLE 4

Titration of Indium With a Solution of $Na_4[Fe(CN)_6]$ in the Presence of Various Salts and Acids

Taken			Found
impurity, in g		In^{3+}, in g	In^{3+}, in g
NaCl	0.5	0.010	0.010
NH_4Cl	0.5	0.010	0.010
Na_2SO_4	0.5	0.010	0.010
$(NH_4)_2SO_4$	0.5	0.010	0.010
Tartaric acid	3	0.010	0.013
Oxalic acid	3	0.010	0.0087
Citric acid	3	0.010	0.010
Phosphoric acid	3	0.010	0.002

During titration of indium chloride solutions of varying concentrations with sodium ferrocyanide, as is evident from Table 2, there was observed a potential jump at the point corresponding to a ratio of $Na_4[Fe(CN)_6] : InCl_3 = 0.75$, i.e., when formation of a precipitate of $In_4[Fe(CN)_6]_3$ was complete. An increase in acid concentration has a deleterious effect on the titration, in that it smooths out the potential jump.

We tried to use diphenylamine as the indicator for the titration of indium with a solution of $Na_4[Fe(CN)_6]$. Diphenylamine in acid solution, under the effect of an oxidizing agent, changes into colorless diphenylbenzidene and is then oxidized to violet diphenylbenzidene [5]. In strongly acid solutions, some of the diphenylbenzidene may be oxidized further, before all the diphenylamine has been converted into diphenylbenzidene.

Titration of indium in the presence of acetic, hydrochloric, nitric, and sulfuric acids, showed that sulfuric acid is the most suitable for titration. A stable, and fairly intense color develops in the course of two to three minutes in 5% H_2SO_4. Titration should be carried out in the cold.

The results obtained (Table 3) show that determination of indium by this method is accurate enough. The best results are obtained on titrating 0.02-0.005 g of indium in 50 ml of solution.

Results for titration of indium in synthetic mixtures of a complex nature, which are met with in various cases of analytical chemistry, are given in Tables 4 and 5. As these results show, the presence of small amounts of chlorides and sulfates in solution does not interfere with titration, but the indicator color develops considerably slower (five to ten minutes). Oxalic acid, when present, depresses the color intensity somewhat; phosphoric acid interferes.

TABLE 5

Titration of Indium With a Solution of $Na_4[FE(CN)_6]$ in the Presence of Various Cations (Original Volume 25 ml)

2.5 mg of the chlorides or sulfates taken in each case							In^{3+} taken, in mg	In^{3+} found, in mg
Be	Ca	Mg	Mn	Al	Ga	La	2.5	2.6
Be	Ca	Mg	Mn	Al	Ga	La	5.0	5.3
Be	Ca	Mg	Mn	Al	Ga	La	10.0	10.0
Be	Ca	Mg	Mn	Al	Ga	La	15.0	15.0
Cd	Mo	U	Tl	Th			5.0	5.0
Cd	Mo	U	Tl	Th			5.0	5.2
Co	Ni	Zn					5.0	5.2
V							5.0	5.1
Ge							5.0	5.1

The presence in solution of many cations (in the form of their chlorides and sulfates) has no effect on titration. Chromium, tungsten, copper, and large amounts of iron interfere.

Zinc, cobalt, aluminum, and tin also give a color in the presence of diphenylamine, but their deleterious influence was successfully eliminated by addition of 3 to 5 g of citric acid to 50 ml of the test solution.

Taking into account the facts given above, the following technique was developed for determining indium by means of $Na_4[Fe(CN)_6]$.

To 50 ml of a solution of an indium salt in 5% sulfuric acid is added 2 drops of a 1% solution of potassium ferricyanide and 2 drops of 1% diphenylamine in concentrated sulfuric acid. In the presence of materials which interfere, 5 g of citric acid is added, and the solution titrated in the cold with $Na_4[Fe(CN)_6]$ solution until the color disappears in the course of 30 seconds; in the presence of cobalt, nickel, zinc, germanium, and vanadium, titration should be carried out to the first decolorization of the solution. The concentration of $Na_4[Fe(CN)_6]$ is checked by titration with potassium permanganate.

Photometric Determination of Indium

The intensity of the color which develops on addition of potassium ferricyanide and diphenylamine to the diluted solution of indium is proportional to the indium concentration. On this basis a photometric determination of small amounts of indium was carried out. The most favorable medium for photometric measurements is 5% H_2SO_4. Results for determination of indium are given in Tables 6 and 7.

As the results obtained show, the minimum amount of indium which can be determined by means of the recommended method is $4 \cdot 10^{-6}$ g in 25 ml of solution. The method can be used for the determination of indium in the presence of Be, Ca, Mg, La, Cd, Ga, Tl, U, Th, Al, Co, Ni, Zn and Mn.

In the presence of zinc, the color of indium develops immediately and is considerably more intense; after ten minutes, however, it corresponds to that of the standard.

The amount of indium found, as is evident from Table 7, in most cases corresponds to the amount taken.

TABLE 6

Photometric Determination of Indium (Volume of solution 25 ml)

In^{3+} taken, in mg	In^{3+} found, in mg	In^{3+} taken, in mg	In^{3+} found, in mg
0.04	0.04	1.0	1.0
0.1	0.1	1.4	1.4
0.2	0.2	2.0	2.0
0.3	0.3	3.0	2.8
0.4	0.38	4.0	3.8

TABLE 7

Photometric Determination of Indium in the Presence of Impurities (In^{3+} taken, 0.25 mg in 25 ml)

Content of impurity in 25 ml of solution, in mg	In^{3+} found, in mg	Content of impurity in 25 ml of solution, in mg	In^{3+} found, in mg
Be − 2.5	0.25	Th − 2.5	0.25
Ca − 2.5	0.25	Al − 2.5	0.23
Mg − 2.5	0.25	Co − 1.0	0.27
Mn − 2.5	0.25	Ni − 2.5	0.25
La − 2.5	0.25	Zn − 2.5	0.27
Cd − 2.5	0.25	V − 2.5	0.25
Ga − 2.5	0.25	Mo − 2.5	0.25
Tl − 2.5	0.25	Ge − 2.5	0.25
U − 1.0	0.25		

The deviations sometimes observed are insignificant when one bears in mind that impurities are present and the amount of indium is small. Cr, Ni, Cu, Fe, and Tl interfere with indium determination.

For the photometric determination of indium, one drop of a 1% aqueous solution of potassium ferrocyanide is added to the solution of the indium salt; this is followed by one drop of a 1% solution of diphenylamine in concentrated sulfuric acid. After five to ten minutes, the color obtained is compared with those of a series of standards prepared under the same conditions. In the presence of impurities, 3-5 g of citric acid is added to both the test and standard solutions. In the presence of cadmium, cobalt, zinc, and uranyl, the color should be compared with that of the standard after 8-10 minutes.

SUMMARY

A titrimetric method is proposed for the determination of indium by means of Na$_4$[Fe(CN)$_6$]; the method is based on the formation, during titration, of a precipitate of the normal ferrocyanide of indium In$_4$[Fe(CN)$_6$].

A photometric method has been developed for the determination of small amounts of indium by means of a mixture of K$_3$[Fe(CN)$_6$] and diphenylamine.

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SEPARATION OF THORIUM FROM THE RARE EARTHS BY MEANS OF PYRIDINE AND PYRIDINE NITRATE

E.A. Ostroumov

In a previous article [1] we showed that it is possible to separate thorium quantitatively from manganese, nickel, cobalt, copper, zinc, and cadmium by means of pyridine. Naturally, the question arises as to whether or not it is possible to separate thorium from the rare earths. The behavior of the latter toward pyridine has only been studied to a very limited extent. Jefferson [2], without adducing any definite proof, notes the quantitative precipitation of cerium (the valency of cerium is not given) and the incomplete precipitation of lanthanum, neodymium, and praseodymium. Watters and Kolthoff [3] point out that quadrivalent cerium is quantitatively coprecipitated with ferric hydroxide during precipitation with pyridine. Trivalent cerium is quantitatively coprecipitated with ferric hydroxide under conditions where the amount of ferric oxide is four times that of the cerium. In the method we have described for precipitation of metal hydroxides by means of pyridine [4], the pH was established at about 6.5.

The pH values at which the hydroxides of some of the metals we were interested in, according to Britton's results [5], are given in Table 1. It might be assumed that during separation of the hydroxides by means of pyridine, when the solution has a pH of about 6.5, precipitation of the rare-earth hydroxides is not quantitative. It was necessary to check our assumptions carefully; in addition, it was desirable to find conditions whereby differences in the pH values at which the hydroxide of thorium and the hydroxides of the rare earths separate out could be used for the quantitative separation of thorium from these elements.

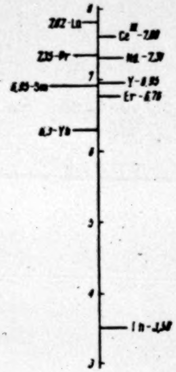
For these experiments, solutions of thorium nitrate and of the nitrates of the rare earths were prepared; these included the nitrates of cerium, yttrium, lanthanum, neodymium, praseodymium, erbium, samarium, and ytterbium; the solutions were standardized gravimetrically.

On carrying out the deposition of rare-earth hydroxides by means of pyridine under the usual conditions, i.e., by heating in the presence of about 6 g ammonium nitrate or chloride, it was found that about 50% was precipitated. Precipitation by means of pyridine in the absence of ammonium salts, although it led to a greater percentage precipitation, nevertheless did not yield quantitative results.

In order that during precipitation of thorium hydroxide the hydroxides of the rare earths were not precipitated, it was found necessary to lower the concentration of OH^- ions, i.e., to lower the pH of the solution, but nevertheless the pH still had to be kept within certain limits to ensure complete precipitation of thorium hydroxide. It was found most expedient to use pyridine in the presence of pyridine nitrate. As shown already [6, 4], such a solution permits accurate regulation of the pH of the medium during precipitation, and gives a pH of about 4.1-4.2.

The precipitation reagent – a solution of pyridine mixed with its nitrate – was prepared as follows: to 20 ml of distilled nitric acid sp.gr. 1.32-1.33 (or 15 ml of nitric acid sp.gr. 1.40) measured out from an accurate cylinder, was added an approximately equal volume of water; this was followed by 34 ml of pyridine which was thoroughly mixed in; the solution was finally made up to 100 ml with water.

Preliminary experiments showed that it is desirable to precipitate thorium in the presence of ammonium nitrate which favors the formation of a denser precipitate of thorium hydroxide, and favors rapid settling out of such precipitates. 6 g of ammonium nitrate was added to the solution of thorium nitrate and the volume made up to about 100 ml with water; the solution was then heated to 80°. The solution was neutralized with 10% ammonia solution, the latter being added dropwise with constant agitation until a weak turbidity appeared. 5-6 drops of nitric acid sp.gr. 1.4 was then added, and the solution stirred to get rid of the turbidity; the liquid was then brought to the boil and, having removed the beaker from the source of heat, thorium hydroxide was precipitated by adding 15 ml of the reagent mentioned above dropwise from a dropping funnel, with constant agitation. Having covered the beaker with a watch glass, the solution was again brought to incipient boiling and, having removed the beaker from the source of heat, it was transferred to a boiling-water bath for the precipitate to coagulate and settle down; it was left there for 30 minutes.



pH values at which various hydroxides separate out according to Britton.

The precipitate was filtered off, washed a few times with hot 3% ammonium nitrate containing a small amount of the precipitation reagent (5 ml of reagent to 100 ml of the 3% ammonium nitrate). The filter paper plus precipitate were then dried and ashed in a porcelain crucible; the residue was finally calcined in an electric oven until the thorium dioxide obtained was of constant weight.

The experimental results (Table 1) show that thorium is removed quantitatively when the conditions indicated are used. As noted already, the pH of the solution was maintained at approximately 4.1-4.2 during the precipitation.

Since the thorium hydroxide is precipitated in a very dense form, while the pH maintained during precipitation is fairly low, one would expect that in such a way it should be possible to separate thorium from the rare earths. We mixed a solution of a thorium salt with a solution of a salt of one of the rare earths and carried out precipitation as described above. The thorium hydroxide precipitate was washed very carefully.

TABLE 1

(Volume of Solution about 120 ml)

ThO_2 taken, in g	ThO_2 found, in g	Error in ThO_2, in g	ThO_2 taken, in g	ThO_2 found, in g	Error in ThO_2, in g
0.0010	0.0011	+0.0001	0.0102	0.0104	+0.0002
0.0010	0.0010	±0.0000	0.0512	0.0512	±0.0000
0.0051	0.0050	−0.0001	0.0512	0.0510	−0.0002
0.0051	0.0053	+0.0002	0.1024	0.1022	−0.0002
0.0102	0.0101	−0.0001	0.1024	0.1025	+0.0001

TABLE 2

(Volume of Solution about 120 ml)

Taken, in g		ThO_2 found, in g	Error in ThO_2, in g	Taken, in g		ThO_2 found, in g	Error in ThO_2, in g
ThO_2	Ce_2O_3			ThO_2	Ce_2O_3		
0.0010	0.1010	0.0010	±0.0000	0.0512	0.0050	0.0512	±0.0000
0.0010	0.1010	0.0009	−0.0001	0.1024	0.0010	0.1023	−0.0001
0.0051	0.0505	0.0049	−0.0002	0.1024	0.0010	0.1024	±0.0000
0.0051	0.0505	0.0052	+0.0001	0.1024	0.0005	0.1025	+0.0001
0.0102	0.0101	0.0103	+0.0001	0.1024	0.0005	0.1024	±0.0000
0.0102	0.0101	0.0101	−0.0001	0.1024	0.1010	0.1025	+0.0001
0.0512	0.0050	0.0511	−0.0001	0.1024	0.1010	0.1023	−0.0001

Table 2 contains the results obtained during separation of thorium from cerium. The amount of thorium dioxide obtained after calcining the hydroxides precipitated, differed only very insignificantly from the amounts taken. The deviations in weight did not exceed the normal errors of weighing. The thorium oxide was pure white in color. In order to check for small amounts of cerium in the precipitated thorium oxide, the latter was fused with sodium pyrosulfate and, after leaching with dilute sulfuric acid, the hydrogen peroxide test for cerium was applied. No cerium was found in any of the tests.

Table 3 contains the results obtained during separation of thorium from other rare earths. Variations in the weight of thorium dioxide were found to be negligible also during separation of thorium from yttrium and lanthanum. The thorium dioxide obtained was pure white in color; in these cases, however, the white color could not be used for assessing the purity of the thorium dioxide since yttrium and lanthanum oxides are also white in color. A spectroscopic examination of the thorium dioxide for the presence of small amounts of yttrium and lanthanum showed that the amount of both yttrium and lanthanum oxides did not exceed 0.0001 g. During separation of thorium from neodymium and praseodymium, errors in the determination of thorium did not exceed weighing errors. The thorium oxide was again white in color. The latter indicates a high degree of purity for the thorium dioxide, since (as tests showed) the presence of 0.0001 g of neodymium or praseodymium oxide in 0.05 g of thorium dioxide was sufficient to give a clearly discernible color. Accordingly, if the thorium hydroxide traps neodymium or praseodymium to any extent during precipitation, the amounts of the latter involved must be less than 0.0001 g. During separation of thorium from erbium, samarium, and ytterbium, the amounts of thorium dioxide actually found deviated very insignificantly from the expected amounts, and the errors involved were very small. The thorium dioxide obtained was pure white in color, indicating that contamination by erbium oxide (if there was any there) was negligible. Less than 0.0001 g of ytterbium could be found spectroscopically, while samarium could not be detected.

TABLE 3

(0.0512 g of ThO_2 taken)

Amount of rare-earth oxide added, in g		ThO_2 found, in g	Error in g ThO_2
Y_2O_3—	0.0051	0.0511	−0.0001
	0.0051	0.0512	±0.0000
	0.0510	0.0513	+0.0001
	0.0510	0.0512	±0.0000
	0.1020	0.0511	−0.0001
	0.1020	0.0513	+0.0001
La_2O_3—	0.0050	0.0513	+0.0001
	0.0050	0.0511	−0.0001
	0.0501	0.0513	+0.0001
	0.0501	0.0510	−0.0002
	0.1002	0.0512	±0.0000
	0.1002	0.0513	+0.0001
Nd_2O_3—	0.0051	0.0512	±0.0000
	0.0051	0.0514	+0.0002
	0.0510	0.0512	±0.0000
	0.0510	0.0510	−0.0002
	0.1020	0.0511	−0.0001
	0.1020	0.0511	−0.0001
Pr_2O_3—	0.0054	0.0513	+0.0001
	0.0054	0.0513	+0.0001
	0.0537	0.0511	−0.0001
Pr_2O_3	0.0537	0.0514	+0.0002
	0.1074	0.0513	+0.0001
	0.1074	0.0512	±0.0000
Er_2O_3—	0.0050	0.0513	+0.0001
	0.0050	0.0511	−0.0001
	0.0502	0.0513	+0.0001
	0.0502	0.0510	−0.0002
	0.1004	0.0511	−0.0001
	0.1004	0.0511	−0.0001
Sm_2O_3—	0.0050	0.0513	+0.0001
	0.0050	0.0512	±0.0000
	0.0498	0.0512	±0.0000
	0.0498	0.0513	+0.0001
	0.0996	0.0512	±0.0000
	0.0996	0.0511	−0.0001
Yb_2O_3 –	0.0047	0.0511	−0.0001
	0.0047	0.0512	±0.0000
	0.0473	0.0510	−0.0002
	0.0473	0.0513	+0.0001
	0.0946	0.0511	−0.0001
	0.0946	0.0512	±0.0000

It is evident, therefore, that even one precipitation of thorium hydroxide by means of a reagent consisting of a mixture of pyridine and pyridine nitrate makes it possible, under the conditions indicated, to carry out a practically complete separation of thorium from the rare earths.

Since, in certain cases, the rare earths taken individually behave somewhat differently than when they are taken together, we decided to carry out a series of tests on the separation of thorium from mixtures of rare earths. The experimental conditions used were the same as before.

As is evident from Table 4, the errors involved during determination of thorium dioxide were very insignificant. The thorium dioxide was pure white in color; no cerium could be detected in it by chemical means. Spectroscopic examination gave the following results: yttrium oxide – less than 0.0001; lanthanum oxide – less than 0.0001; ytterbium oxide – less than 0.0001; samarium oxide – not detected. The pure white color of the

TABLE 4

The Following Amounts were Taken: 0.0202 g Ce_2O_3, 0.0204 g Y_2O_3, 0.0200 g La_2O_3, 0.0204 g Nd_2O_3, 0.0214 g Pr_2O_3, 0.0200 g Er_2O_3, 0.0200 g Sm_2O_3 and 0.0207 g Yb_2O_3

ThO_2 taken, in g	ThO_2 found, in g	Error in ThO_2, in g
0.0512	0.0513	+0.0001
0.0512	0.0511	−0.0001
0.1024	0.1022	−0.0002
0.1024	0.1024	±0.0000

thorium dioxide showed that contamination by neodymium and praseodymium (if they were there at all) was negligible and less than 0.0001 g.

Experimental procedure. Usually, thorium, cerium and the rare earths are isolated as their oxalates, which by careful calcination are converted into the oxides. The mixture of oxides is dissolved on heating in nitric acid sp.gr. 1.5; the solution is evaporated in a porcelain dish on a water bath to dryness, a few drops of alcohol being added to convert cerium to the trivalent form. The residue is moistened with a small amount of nitric acid, some water is then added and the whole thoroughly mixed. Thorium is removed as the hydroxide from the solution obtained, as follows.

The solution is diluted with water so that 100 ml of solution contains not more than 0.2 g of thorium dioxide. To about 100 ml of the solution is added 6 g of chemically pure ammonium nitrate, and the solution heated to 80°, after which it is neutralized with 10% ammonia solution, the latter being added dropwise, with constant agitation, until a slight turbidity appears. Five to six drops of nitric acid sp.gr. 1.4 is then added to remove the turbidity. The liquid is next brought to the boil and, having removed the beaker from the source of heat, thorium is precipitated as the hydroxide by adding dropwise from a dropping funnel, with careful agitation, 15 ml of reagent consisting of the mixture of pyridine and pyridine nitrate.

The beaker is covered with a glass and the solution again heated to incipient boiling and, having removed the beaker from the source of heat, it is transferred to a boiling-water bath for the precipitate to coagulate and settle out over a period of 30 minutes. The precipitate is filtered off and washed with hot 3% ammonium nitrate containing some of the precipitation mixture (5 ml of the latter to 100 ml of ammonium nitrate).

Filter paper plus precipitate are dried and ashed in a platinum or porcelain crucible; the residue — thorium dioxide — is finally calcined in an electric oven to constant weight.

Experiments have shown that one precipitation of thorium as the hydroxide is sufficient to separate this element from the rare earths; usually there is no need to resort to reprecipitation.

When very large amounts of the rare earths are present, the thorium isolated can be reprecipitated. When this has to be done, the filter paper plus thorium hydroxide are carefully ashed in a porcelain crucible; they are then calcined at a low temperature to burn off the carbon, the oxide obtained is dissolved in nitric acid sp. gr. 1.5, and precipitation repeated as described above. The method can also be used in preparative work.

SUMMARY

Thorium is quantitatively precipitated by means of a mixture of pyridine and its nitrate at a pH of 4.1-4.2. Ammonium nitrate accelerates coagulation and settling out of the precipitate. Thorium hydroxide is precipitated in a very dense form which exhibits a very low absorptive capacity. Yttrium, lanthanum, trivalent cerium, neodymium, praseodymium, erbium, samarium, and ytterbium remain in solution.

Thorium is precipitated in such a pure state that reprecipitation is not necessary.

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A STUDY OF A PHOTOMETRIC METHOD OF DETERMINING CERIUM AS THE PEROXIDE COMPLEX

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For the photometric determination of cerium, of the greatest importance is the method based on the formation of a colored compound by the action of hydrogen peroxide in an alkaline medium [1-4]. This method permits determination of cerium in the presence of other rare earths. The latter are precipitated as a whole in the form of oxalates; the precipitate of the latter is then dissolved by some method or other, after which cerium is determined. Formation of a colored compound occurs in nitrate and alkali media [2, 5, 7], or in ammonia [6], as well as in a medium of a 50% solution of potassium carbonate [2, 5, 7].

The experiments we have carried out on the methods recommended confirmed the reproducibility and specificity of the formation of a colored compound. The reaction is also characterized by high sensitivity [3, 4]. On measuring the light absorption on an FEK-M photocolorimeter using a blue-light filter and a 2 cm cell, we found that the molar absorption coefficient Q_m is equal to approximately 800.

At the same time the methods described in the literature suffer from some serious disadvantages. The most important drawback is that the colored peroxide compound of cerium is insoluble in water. Plank [1], who was the first to suggest the methods under consideration, carried out determinations in a medium of concentrated potassium carbonate solution without using hydrogen peroxide, cerium being oxidized by atmospheric oxygen. Plank noted that addition of hydrogen peroxide gives a more rapid color effect, nevertheless, under such conditions a precipitate separates out. In more recent work [3, 4] the workers have not considered this point, and have not adopted any special measures for eliminating the effect of solid phase formation. Experiments have shown, however, that this last factor presents the greatest difficulty. Even when the recommended procedures are strictly adhered to, usually after a short time (0.5-3 minutes) a turbidity develops or a precipitate separates out. Comparison of colors in a colorimeter or in a photocolorimeter often becomes completely impossible.

Experiments have shown that formation of the colored peroxide compound of cerium is strongly dependent on the acidity of the solution. It is practically impossible to find a favorable alkalinity range. In acid medium, and also at a pH of 7 or 8, the color is attenuated or does not appear at all, while at pH 8 or 9 and above, coagulation or turbidity of the solution is observed.

Riabchikov and Strelkova [3] recommend that for each test solution one should take a series of samples and experimentally choose the amount of 0.1 N NaOH, in which (in the presence of H_2O_2) the colored compound is formed, but in which no precipitate separates out. Using this technique we succeeded in preparing solutions for measurement of the optical density of the colored complex. Nevertheless, in the course of ordinary analysis, solutions are obtained which differ in their initial acidity and, accordingly, a lot of time and test solutions are used up in establishing the amount of alkali necessary for each separate solution. Attempts which we made to simplify this technique, for example by controlling the pH by means of indicator papers, did not yield positive results.

The Use of Glycerol for Stabilizing Cerium Peroxide Suspensions

The first problem was to find a method for preparing sufficiently stable solutions of the colored peroxide complex of cerium. For this purpose we tested various media. Thus, we studied the action of a series of water immiscible organic solvents for extracting the complex. We were, however, unable to find such a solvent; it was observed that many, in particular isoamyl alcohol, readily float the peroxide complex of cerium. Next, various materials which give soluble complex compounds with hydrogen peroxide (urotropine, urea, etc) were tested. These materials, however, showed no observable effect. Various stabilizers were tested with the intention of keeping the colored complex in a state of suspension. It was found that gelatine, starch, gum-arabic, and a number of other materials exhibit no appreciable stabilizing effect. It was found, however, that glycerol is a good stabilizing agent. Citrate solutions in which a turbidity develops, on following the procedures usually recommended, were clear and suitable for photometric measurements when about 20% by volume of glycerol was added beforehand. Experiments showed that glycerol only acts as a stabilizing agent in the presence of a complexing agent. Addition of gylcerol alone (e.g., without citrate or a complexon) does not give a transparent colored solution.

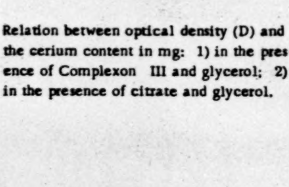
Tests also showed that increasing the amount of citrate increases the stability of the colloidal suspension somewhat. At the same time, a large amount of citrate complexes part of the cerium and prevents formation of the colored peroxide compound, thereby leading to a decrease in optical density. The solutions used in these measurements were prepared as follows. To 1 ml lots of an almost neutral solution containing 5 mg of cerium as the nitrate, were added various amounts of a saturated solution of sodium citrate, these were followed in succession by 1 ml of 0.1 N NaOH, 0.25 ml of 10% H_2O_2, and the volumes made up to 50 ml with water. Optical density was measured on an FEK-M apparatus using a blue filter and a 3 cm cell. The results of one such series is given below.

Number of milliliters of saturated citrate solution	2	5	10	20
Optical density	0.79	0.59	0.33	0.028

Thus, on increasing the citrate concentration, the optical density drops considerably (2-20 times).

In the literature [3, 5] it is recommended that the oxalate precipitates of the rare earths be treated on the filter with a saturated solution of sodium citrate until the oxalates dissolve completely. The results just given show that during this process it is necessary, at least, to fix the amount of citrate in the test and standard solutions accurately.

We obtained satisfactory results on using glycerol. Experiments were carried out according to the following procedure. The original solution used was one of $Ce(NO_3)_3$ acidified slightly with nitric acid and containing 5 mg of cerium per ml. 0.1 to 1 ml lots of this solution corresponding to cerium contents ranging from 0.5-5 mg were chosen for photometric measurements. The cerium solution was transferred to a 50-ml standard flask, to which was then added two drops of a saturated solution of sodium or potassium citrate, 1 ml of 0.1 N NaOH, 20 ml of glycerol (1 : 1), and five drops of 10% hydrogen peroxide solution. Formation of the colored compound requires five to eight minutes. Water was then added to bring the volume up to the mark, and the solution allowed to stand for a few minutes to let oxygen bubbles escape. Measurements were carried out as indicated above. The results obtained are shown on the diagram, Curve 2.



Relation between optical density (D) and the cerium content in mg: 1) in the presence of Complexon III and glycerol; 2) in the presence of citrate and glycerol.

Solutions not containing glycerol were prepared for comparison. In these cases, the optimum amount of 0.1 N NaOH was established beforehand in each case. The following procedure was adopted in order to do this. Known amounts of cerium were introduced into a series of 50-ml standard flasks; 1, 2, 3, etc. drops of 0.1 N alkali was then added and the procedure given in [3] then followed. A scale was thereby obtained in which the color intensity increased right up to the appearance of turbidity. In order to construct a curve, the value of the optical density corresponding to a cerium solution which had the maximum color, but in which turbidity had not yet appeared, was taken. Since, as already mentioned above, such a method of preparing solutions is not convenient for analysis, we only used this method for studying the effect of various factors. Results of optical density measurements were approximately 8% higher than those obtained when glycerol was used. Thus, glycerol depresses the sensitivity of the method slightly. Nevertheless, the stability of the colored solution with time increases considerably, and preparation of such solutions does not take long. The use of glycerol has the added advantage that the color intensity is independent of the volume of solution before addition of the H_2O_2. When glycerol was not used, it was observed that during the photometric determinations, the color weakened when the solution of the cerium salt was diluted before addition of H_2O_2.

Choice of Complexing Agent and the pH of the Medium

Comparison of various complexing agents showed that ethylenediamine tetracetic acid is the most convenient to use. When the reaction is carried out under those conditions normally recommended, the colored compound coagulates in 0.5-5 minutes. In the presence of Complexon III there is formed a colored cerium complex which is characterized by a high degree of dispersion, so that even in the absence of glycerol, there is formed a suspension which is stable over a period of several hours. In the presence of glycerol and Complexon III, the colloidal suspension is stable for an even longer time.

It was pointed out above that the colored cerium complex is very sensitive to the pH of the medium. Even when glycerol was used, it was observed that insufficient ammonia strongly restrains color development, while a large excess of ammonia leads to opalescence. When insufficient alkali is present, the color, in addition, gets stronger with time. In order to avoid these phenomena, it is expedient to use a buffer solution with a pH of 9 (20 g ammonium chloride and 100 ml of concentrated ammonia were diluted to 1 liter).

The use of Complexon III and a buffer solution permits one, in the ordinary course of analysis, to do without glycerol. Buffer solution in amounts ranging from 1 to 10 ml on 50 ml of total volume has no effect on the value of the optical density. Nevertheless, increasing the amount of Complexon leads to a decrease in optical density; this is similar to the phenomenon described above in the case of the citrate. Thus, for a cerium content of 1 mg in 50 ml, the optical density in the presence of 2, 5, and 10 ml of 0.1 N Complexon III is 0.248, 0.232, and 0.201 respectively. The presence of a large amount of salts in solution weakens the color and decreases the stability of the colored suspension. In these cases it is best to use glycerol.

On the basis of the facts given above, we have developed the following procedure for the photometric determination of cerium. To solutions containing from 0.5-5 mg of cerium in the form of its citrate or chloride, are added 2 ml of 0.1 N Complexon III solution, 10 ml of glycerol (1:1), and the solution neutralized with ammonia until it has a faint smell of the latter (or until litmus paper turns blue); 5 ml of buffer solution and five drops of 10% hydrogen peroxide are then added. After five minutes the volume is made up to the mark with water, the whole thoroughly mixed and, after 20-30 minutes, colorimetric measurements carried out using a blue filter and a 2 cm cell; water is used as reference. The results obtained are shown on the diagram, Curve 1.

Dissolving Rare Earth Oxalates

Usually cerium is determined on the precipitate of rare earth oxalates taken as a whole. It is often recommended that these oxalates be brought into solution by calcining them to form the oxides, and then dissolving the latter in acids. It is known, however, that calcined cerium is difficult to dissolve in acids. Some procedures recommend that the oxalates be dissolved in excess complexing agent (citrate). Nevertheless, the latter, as shown above, complicates formation of the colored cerium compound. In this connection therefore we attempted to dissolve the rare-earth oxalates by means of acid with addition of persulfate or permanganate for oxidizing the oxalate ions.* For this purpose the precipitated oxalates were washed off the filter paper with water containing sulfuric or nitric acid, persulfate or permanganate was then added and the solution boiled. Excess of persulfate was destroyed by boiling, while excess permanganate was destroyed by addition of a few drops of hydrogen peroxide.

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*The oxalates can also be converted into soluble chlorides by evaporating calcium and rare-earth oxalates a few times with aqua regia.

Of the two oxidizing agents tested, permanganate proved to be the best. Hydroxylamine can be used to keep manganese in solution during precipitation of rare-earth hydroxides by means of ammonia (for separating them from calcium).

The photometric method described has been used for many determinations of cerium in solutions of its pure salts and in synthetic mixtures containing aluminum and iron salts, after precipitation of cerium as the oxalate both with and without calcium, the oxalates being broken up by ashing and by oxidation with persulfate or permanganate. Cerium which ha been added to natural samples containing the rare earths was determined in the same way.

Work with synthetic mixtures showed that the error in the photometric determination of cerium in pure solutions of its salts is about ±5% (relative), which is not in excess of normal errors obtained during photometric determinations. After precipitation of cerium as the oxalate (either with or without a collector), and also during the analysis of mixtures containing 1-5 mg of cerium (as the nitrate) and 100 mg of iron or aluminum (as alum), after all the separation operations involved as described in the procedure, the deviation was slightly greater than ±6% relative; the maximum deviation was up to 20% relative. Under these conditions, the number of negative errors increase, this being determined by losses in cerium during the separation operations. Thus, of 26 experiments, only nine gave a positive error.

Cerium was subsequently determined by the procedure given below in natural materials containing 0.06-0.3% of cerium dioxide. During this series, cerium was added artificially to some of the samples. Comparison of the results of analysis on samples with and without addition of cerium indicated analogous results.

Photometric determination was carried out by the following technique. 1 g of test material was broken down with a mixture of hydrofluoric and sulfuric acids. The dry residue was treated with HCl (1: 1) and the mixture heated; it was then transferred to a beaker and allowed to stand overnight. The insoluble residue was filtered off; when this residue had a dark color, it was given a second treatment with hydrofluoric and sulfuric acids, or fused with sodium carbonate, the dry residue was again dissolved in HCl (1: 1), the solution filtered and the filtrate combined with the first filtrate.

The combined filtrates were evaporated and the hydroxides precipitated by means of ammonia. When aluminum was present, precipitation was carried out with the aid of sodium hydroxide in order to remove the aluminum from the rare earths. The precipitate was filtered and, without washing in situ, was washed into a beaker, 2-4 ml of a 5% solution of calcium chloride was added to the solution, followed by an equal volume of a solution of oxalic acid saturated with respect to the latter in the cold; the mixture obtained was heated almost to the boiling point. Using "universal indicator," ammonia was added until a pH of 3 was attained; the solution was then left to stand overnight. The oxalates were reprecipitated, since at high iron and aluminum contents, the oxalate precipitates trap part of these elements.

The rare-earth oxalates together with the collector – calcium oxalate – were filtered off and washed four to five times with a 1% oxalic acid solution; the precipitates were then carefully ashed at 500-600°, or dissolved in acid containing permanganate, as indicated above. The rare-earth hydroxides were separated from calcium by means of ammonia. The precipitate of hydroxides was dissolved in HCl on the filter. The hydrochloric acid solution was then used for photometric determinations, the latter being carried out as described above.

SUMMARY

A study has been made of the requisite conditions for the photometric determination of cerium as the peroxide complex. The main difficulty of the methods formerly advocated has been precipitation of the colored cerium compound. It is now suggested that the solution be stabilized by means of glycerol in the presence of Complexon III. When the latter is used, a highly dispersed form of the colored cerium complex is obtained and there is no need for a stabilizer.

It has been shown that it is possible to bring rare-earth oxalates into solution without calcining them; the alternative method suggested here is to dissolve the oxalates directly in sulfuric acid to which persulfate has been added, or in nitric acid containing permanganate.

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PHOTOMETRIC DETERMINATION OF CERIUM AS CERIUMMOLYBDIC HETEROPOLY ACID

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Of the published methods for the photometric determination of small amounts of cerium, the most sensitive and widely used method is that based on formation of a colored complex with hydrogen peroxide in the presence of nitrates [1, 2], or carbonates [3, 4]; the persulfate [5], and the persulfate-brucine methods [6, 7], with benzidene [8, 9], gallic acid [10], alcohols [11], and veratrol [12], are all either of low sensitivity or are difficult to carry out. The essential drawback of the method involving hydrogen peroxide is the necessity for a preliminary separation of cerium from the heavy metals and molybdenum. Accordingly, we tried to develop a new method for the photometric determination of cerium which is based on the formation of the ceriummolybdic heteropoly acid.

First of all,experiments were carried out to try and establish the optimum conditions for the formation of the ceriummolybdic heteropoly acid.

1. Effect of molybdate concentration. Complete formation of the ceriummolybdate complex depends on excess molybdate in solution. The effect of sodium molybdate concentration at a hydrogen ion concentration equivalent to 0.2 N on completeness of formation of the ceriummolybdate complex was studied. To 1 ml of $Ce(SO_4)_2$ solution containing 0.20 mg of Ce, was added 0.54 ml of sulfuric acid (sp.gr. 1.115) to give a sulfuric acid concentration in the final solution of 0.2 N, and various amounts of a solution of sodium molybdate with a pH of 7. The solutions were diluted to 10 ml with water and the optical density of the solutions determined on a FEK-52 photocolorimeter at 360 mμ. The results of these measurements are given on Figure 1. In order to establish the optimum conditions for formation of ceriummolybdic acid, experiments were carried out on the effect of excess reagent (sodium molybdate), at various hydrogen-ion concentrations, on completeness of formation of the complex.

For this purpose, various amounts of sulfuric acid (sp.gr. 1.115) were added to 1 ml of $Ce(SO_4)_2$ solution containing 0.20 mg cerium, followed by a 60, 80, and 100-fold excess of sodium molybdate previously neutralized to a pH of 7. The volume was made up to 20 ml in each case. A solution of sodium molybdate with the same acidity was used as the reference solution. Measurements were made on a SF-4 spectrophotometer.

The results of these measurements are shown in Figure 2. As is evident from Figure 2, the optimum excess of sodium molybdate is a 60-fold excess.

2. Effect of hydrogen ion concentration. In order to find the optimum acid concentration for the formation of the ceriummolybdate complex, various amounts of sulfuric acid, and 5 ml of a 5% solution of sodium molybdate (60-fold excess) were added to a solution of $Ce(SO_4)_2$ containing 1 mg, and the volume of the solutions made up to 10 ml with water; the optical density of the solutions obtained was then measured on a FEK-52 photocolorimeter at 360 mμ.

Water was used as the reference solution. The results obtained are shown in Figure 3.

The color intensity of solutions of the ceriummolybdate complex is considerably higher than that of $Ce(SO_4)_2$ solutions of the same concentration in 0.2-0.6 N H_2SO_4 (Figure 3).

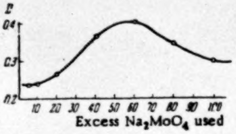

Fig. 1. Effect of sodium molybdate concentration, for a constant hydrogen ion concentration of $H^+ = 0.2$ N, on completeness of formation of ceriummolybdate complex.

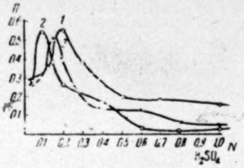

Fig. 2. Effect of excess sodium molybdate, for various hydrogen ion concentrations, on completeness of formation of the ceriummolybdate complex: 1) 60-fold excess of molybdate; 2) 80-fold excess of molybdate; 3) 100-fold excess of molybdate.

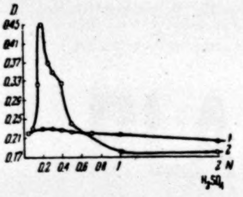

Fig. 3. Relation between the color intensity of cerium sulfate solutions (1), and of ceriummolybdate heteropoly acid solutions (2) and the acidity, for a 60-fold excess of molybdate.

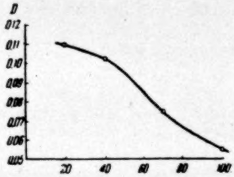

Fig. 4. Relation between the color intensity of the ceriummolybdate heteropoly acid formed and temperature.

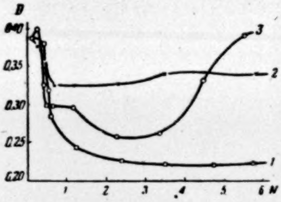

Fig. 5. Change in color intensity of the ceriummolybdate complex formed with changes in hydrogen ion concentration in mineral acids: 1) nitric; 2) sulfuric; 3) hydrochloric.

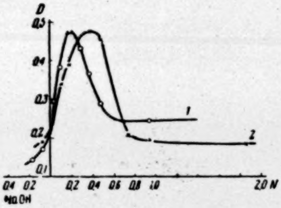

Fig. 6. Stability of the ceriummolybdic heteropoly acid in the presence of sulfuric (1) and perchloric (2) acid.

As Figure 3 shows, the optimum hydrogen ion concentration for the formation of the ceriummolybdic acid is 0.2 N with respect to H_2SO_4.

A Study of the Stability of the Ceriummolybdic Heteropoly Acid

Ceriummolybdic acid, as the results given in the table show, is fairly stable with time.

All the same, the stability of the ceriummolybdate complex changes with changes in temperature (Figure 4). The stability of the ceriummolybdate complex formed with changes in hydrogen ion concentration of the solution was studied as follows.

TABLE

Relation Between Color Intensity of Ceriummolybdic Heteropoly Acid and Time

Time	0	5 min	10 min	15 min	20 min	30 min	40 min	50 min	1 hour	1 hour 15 min	1 hour 25 min
D	0.432	0.430	0.429	0.430	0.432	0.428	0.420	0.419	0.415	0.400	0.400

To a solution of ceriummolybdic acid prepared in 10 ml of 0.2 N H_2SO_4 (0.54 ml H_2SO_4, sp.gr. 1.115, 1 ml of $Ce(SO_4)_2$ containing 0.20 mg cerium, 5 ml of 5% neutral sodium molybdate solution, made up to 10 ml with water), ten minutes after formation of the heteropoly acid, was added water and mineral acid in order to give various acidities. The total volume was 20 ml. The optical density of the solutions was measured on a FEK-52 photocolorimeter at 360 mμ. Water was used as the reference solution. The results of these measurements are shown in Figure 5. As is evident from Figure 5, ceriummolybdic acid breaks down on increasing the hydrogen ion concentration. The special shape of the curve relating the optical density of the solution to increasing hydrochloric acid concentration is determined, obviously, by a side oxidation-reduction reaction. A comparative study of the behavior of the ceriummolybdate complex in media made from sulfuric and perchloric acid showed that the ceriummolybdate complex breaks down with increasing hydrogen ion concentration, and not as a result of the complexing of cerium into a sulfate complex. These results are shown in Fig. 6.

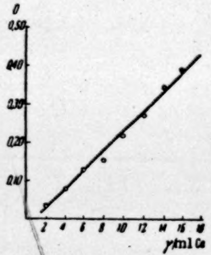

Fig. 7. Calibration curve for determination of 0.025-0.4 mg Ce.

Experiments showed that the ceriummolybdate complex is stable over a narrow hydrogen ion concentration range, namely in media of 0.1-0.3 N H_2SO_4 and in a medium 0.4 N with respect to perchloric acid. Nevertheless, the comparatively narrow hydrogen ion concentration range does not prevent one from using formation of the ceriummolybdate complex for the photometric determination of cerium.

The color intensity of solutions of ceriummolybdic acid conform to Beer's law. A calibration curve for determination of 1-16 γ of Ce/ml in 0.2 N H_2SO_4 is shown in Figure 7. The sensitivity of the reaction is 1 γ Ce/ml.

Cerium can be determined photometrically as follows: to a solution containing 0.025-0.4 mg of cerium is added sulfuric acid until the concentration of the latter in the final volume is 0.2 N, 12 ml of a 5% neutral solution of sodium molybdate is then added (or 10 ml of a 5% solution of ammonium molybdate), and the solution diluted with water to 25 ml; after ten minutes the optical density is measured on a SF-4 spectrophotometer at 380 mμ (slit width 0.4 mm).

SUMMARY

A new method has been developed for the photometric determination of cerium, which is based on the formation of ceriummolybdic heteropoly acid. The conditions of formation and the stability of the ceriummolybdate complex have been studied.

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ANALYTICAL APPLICATION OF PHENOLCARBOXYLIC ACIDS OF THE TRIPHENYLMETHANE SERIES

DETERMINATION OF VANADIUM IN STEELS BY MEANS OF ALUMINON

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In a previous article [1] it was shown that the qualitative reaction for vanadium ions using aluminon, a reaction which had been suggested by V.I. Kuznetsov [2, 3], can be used for the photometric determination of vanadium in pure solutions. The conditions for carrying out this reaction were also described in that article in detail: the relations between the optical density of the solution and the analytical form of test material, pH, temperature, and time were established; the composition of the complex was determined; and the accuracy and reproducibility of the method were established.

TABLE 1

pH Limits for the Interaction of Aluminon With Various Cations (Acetate and acetate-ammoniacal [5] buffer solutions)

Cation, C-1000 γ/ml	Interaction pH range	Color of the reagent at the limits of the pH range		Color of the analytical form
		acid	alkali	
Mo^{VI}	1-4	Rose*	Rose	Raspberry
Cr^{3+}	2-5.5	Rose*	Pale-rose	Red*
Th^{IV}	2-7	Rose*	Colorless	Rose*
Sn^{2+}	2-7	Rose*	Colorless	Rose*
VO^{2+}	2-7	Rose*	Colorless	Raspberry
UO_2^{2+}	2-7	Rose*	Colorless	Raspberry
Al^{3+}	2-9	Rose*	Colorless	Raspberry*
Fe^{3+}	2-9	Rose*	Colorless	Violet*
Ce^{III}	2-9	Rose*	Colorless	Red*
Ti^{IV}	2-11	Rose*	Colorless	Red*
Cu^{2+}	4-9	Rose	Colorless	Raspberry*
Be^{2+}	4-9	Rose	Colorless	Red
Pb^{2+}	6-9	Pale-rose	Colorless	Rose*
Co^{2+}	7-9	Colorless	Colorless	Rose*
Zn^{2+}	7-9	Colorless	Colorless	Rose*
Mn^{2+}	7-9	Colorless	Colorless	Rose*
Cd^{2+}	7-11	Colorless	Colorless	Rose*
Ni^{2+}	9-11	Colorless	Colorless	Rose*
Mg^{2+}	9-11	Colorless	Colorless	Rose*
Ca^{2+}	11 and higher		Colorless	Rose

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*A colored precipitate separates out.

The interaction of the vanadyl ion with aluminon is of considerable analytical importance: it is characterized by a fairly high sensitivity, and occurs rapidly; reaction takes place over a wide concentration range, within which the solution of the reaction product conforms to the Lambert-Beer law; the reagent is fairly readily obtainable.

TABLE 2

Quantitative Determination of VO^{2+} in the Presence of Other Elements

V^{IV} taken, in γ	Me added, in γ	V^{IV} found, in γ	Error, in γ	Ratio V^{IV} : Me	V^{IV} taken, in γ	Me added, in γ	V^{IV} found, in γ	Error, in γ	Ratio V^{IV} : Me
	Ni^{2+}					Ca			
5	5000	5	0	1 : 1000	5	2000	5	0	1 : 400
30	5000	33	–3		100	2000	100	0	
5	10000	5	0	1 : 2000	5	10000	8	+3	1 : 2000
30	10000	30	0		30	10000	31	+1	
90	10000	85	–5		80	10000	90	+10	
	Co^{2+}					Zn^{2+}			
5	5000	5	0	1 : 1000	5	2000	7	+2	1 : 400
70	5000	68	–2		100	2000	100	0	
5	10000	8	+3	1 : 2000	5	5000	7	+2	1 : 1000
60	10000	60	0		30	5000	31	+1	
					100	5000	80	–20	
	Mn^{2+}	5	0	1 : 2000		Cd^{2+}			
5	5000	33	+3		5	1000	6	+1	1 : 200
30	5000	5	0	1 : 2000	80	1000	80	0	
5	10000	62	–8		5	3000	5	0	1 : 500
70	10000				60	3000	75	–15	
	Mg^{2+}					Mo^{VI}			
5	5000	5	0	1 : 1000	5	100	5	0	1 : 20
20	5000	20	0		50	100	52	+2	
100	5000	90	–10		100	100	100	0	
5	10000	7	+ 2	1 : 2000	5	200	8	+3	1 : 40
50	10000	41	– 9		100	200	98	–2	

We studied this reaction further in detail with the aim of using it for the determination of small amounts of vanadium in steels.

Aluminon is not a specific reagent for the vanadyl ion. The specificity of the reaction can be increased by controlling the hydrogen ion concentration. Many organic reagents generally react with various elements only at certain pH values [4]. The pH limits for the reaction of aluminon with various ions are given in Table 1.

It is evident from this table that many ions interact with aluminon at pH values which differ from those for the vanadyl ion. Thus, the alkali and alkaline-earth metals, as well as Mn^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, As^{V}, W^{VI}, Hg$_2^{2+}$, Hg^{2+} do not interfere with the reaction for the vanadyl ion.

The limiting ratios for a number of cations, in the presence of which vanadium can be determined quantitatively by means of aluminon, are given in Table 2.

The results given in Table 2 show that relatively large amounts of such ions as Co^{2+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+} and Cd^{2+} do not interfere with vanadium determination.

All the same, Al^{3+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Be^{2+}, Th^{IV}, Ce^{III}, Ti^{IV}, and UO$_2^{2+}$ form colored compounds with the reagent, in the pH range which is most favorable for vanadium determination. The results given in Table 3 show that some ions are as sensitive to aluminon as the vanadyl ion.

All the facts adduced above indicate that in developing a method for the determination of vanadium in steels by means of aluminon, it is essential to take into account the specificity of the reagent, and to eliminate interference on the part of some of the elements which usually accompany vanadium.

There are fairly reliable methods available for removing interference from iron, the main component of steel; one of these is reduction with ascorbic acid [6]. As for chromium, which is also a steel component, we are unaware of any simple, reliable, and convenient methods for removing this metal from vanadium; usually, they are separated from each other by electrolysis on a mercury cathode [7], by a chromatographic method [8], or by choosing reagents, where chromium does not affect the results of vanadium determination considerably [9].

TABLE 3

Sensitivity of the Reaction Between Aluminon and the Ions of Certain Elements

Cation	VO^{2+}	Al^{3+}	Fe^{3+}	Cr^{3+}	Be^{2+}	Mo^{VI}	Ti^{IV}	Ni^{2+}	Co^{2+}	Th^{IV}	UO_2^{2+}	Cu^{2+}	Mg^{2+}	Ca^{2+}
Sensitivity in γ//ml	0.1	0.05	0.5	25	0.25	25	1.25	0.5	50	2	2.5	0.5	0.5	10
Optimum pH	4	4	3.22	4	4	2.8	4	9	7	4	4	5	11	11

In order to prevent interference by iron and chromium we used thioglycollic acid; this reagent forms a pale-green colored complex with trivalent chromium [10, 11]; on heating in an acetate buffer with a pH of 3.4-3.8, this color becomes appreciably paler.

Table 4 contains results for the determination of vanadium by means of aluminon in the presence of iron and chromium, after addition of thioglycollic acid.

Thus, by adding thioglycollic acid, interference from practically any amount of iron can be eliminated. Chromium, which gives a colored complex with thioglycollic acid, does not interfere with vanadium determination up to a limiting ratio of 1 : 200.

TABLE 4

Determination of Vanadium in the Presence of Iron and Chromium After Masking With Thioglycollic Acid

V^{IV} taken, in γ	Me added, in γ	V^{IV} found, in γ	Error, in γ	Ratio V^{IV}:Me	V^{IV} taken, in γ	Me added, in γ	V^{IV} found, in γ	Error, in γ	Ratio V^{IV}:Me
	Fe^{3+}					Cr^{3+}			
5	500	5	0	1 : 100	5	500	4	−1	1 : 100
25	500	23	−2		40	500	38	−2	
5	1000	7	+2	1 : 200	90	500	90	0	
60	1000	61	+1		5	1000	5	0	1 : 200
5	10000	6	+1	1 : 2000	30	1000	31	+1	
50	10000	49	−1		50	1000	50	0	
100	10000	98	−2		70	1000	67	−3	

In order to prevent interference by iron and chromium, a known amount of a 2.5% solution of thioglycollic acid should be added. The order in which the reagents are added is also of essential importance: a known amount of thioglycollic acid is first added to the test solution, the buffer solution is added next, and, finally, the aluminon solution. In order that the thioglycollic acid does not change the pH of the solution, it is neutralized beforehand with alkali (to Congo Red).

Determination of Vanadium in Steels

0.8-1.0 g* of steel is dissolved in 40-50 ml of HCl (1 : 1) in a porcelain dish covered with a watch glass, by heating on a water bath. The watch glass is removed and the contents of the dish evaporated until the volume is 10-15 ml, 1-2 ml of concentrated HNO_3 is then added and the solution evaporated to dryness. 5-10 ml of HCl (1 : 1) is added to the residue and the whole evaporated to dryness once again.* The residue is moistened two to three times with a small amount of water (15-20 ml), and the solution evaporated to 5 ml, 2-3 ml of a 20% solution of hydroxylamine and 10-15 ml of water are then added. The solution is boiled for 15-20 minutes and then transferred to a 100-ml standard flask. After cooling, the solution is diluted to the mark with water and thoroughly mixed; from an aliquot of this solution the silica is filtered off (through a dry funnel into a dry flask). For determination of the vanadium, 1 ml of this filtered solution is transferred to a 10-ml beaker and 0.15-0.25 ml of a 2.5% solution of thioglycollic acid added, the latter having been neutralized to the Congo Red end point beforehand; the solution obtained is then warmed slightly on a water bath for one to two minutes, it is cooled and 5 ml of buffer solution with a pH of 3.72-3.86 added, followed by 0.3 ml of gum arabic (2%), and the final solution again heated on a water bath for five miuutes. To the cooled solution is finally added 0.5 ml of a 0.25% solution of aluminon; the liquid in the beaker should then have a volume of 6 ml.

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*For vanadium contents less than 0.5%.

TABLE 5

Determination of Vanadium in Steels

Steel sample	Specified vanadium content	Vanadium content as determined by the method developed above	Difference, in %
30-a	0.26	0.27	+0.01
		0.26	0
		0.26	0
		0.25	−0.01
30-b	0.24	0.235	−0.005
		0.24	0
		0.22	−0.02
		0.24	−0
124	0.24	0.23	−0.01
		0.24	0
		0.24	0
No. 1	0.09	0.108	+0.018
		0.09	0

The aluminon solution used was prepared by dissolving the dye on heating for 10-15 minutes on a water bath at 80-90°.

Five minutes after addition of the aluminon the optical density is measured, using a green filter (λ about 530 $m\mu$). The vanadium content is found by means of a calibration curve constructed under the same conditions as those used for the test sample.

The method described above has been widely checked on various types of steel (Table 5) during student practice on the analysis of ferrous and nonferrous metals at Saratov University.

SUMMARY

A photocolorimetric method has been developed for the determination of vanadium in steels of certain grades, without having to resort to preliminary separation of interfering ions.

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* This procedure for getting the sample into solution probably ensures complete breakdown of the vanadium carbides contained in the test steel samples, since the results obtained were in complete agreement with the specified contents.

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A COLOR REACTION FOR URANIUM WITH THE REAGENT ARSENAZO

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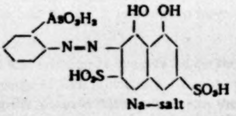
Ions of U^{IV} and U^{VI} form chromophoric atomic groupings; Muller [1] as long ago as 1920 turned his attention to this point. As a consequence of this, color reactions are possible for uranium which are based on its chromophoric action [2]. A number of color reactions for uranium, or more accurately uranyl, described in the literature, belong to this category. All reactions which are based on the use of noncolored reagents belong to this category; they include salicylic [3], sulfosalicylic [4, 5], aminosalicylic [6], gallic [7], resorcylic [7], or para-cresotic [8] acids, tannin [7], pyrocatechol disulfonic acid [9], aminopyrocatechol [6], dibenzoylmethane [10, 11], oxalohydroxamic acid [12], dihydroxyacetophenoneoxime [13], furoacetyl-2,5-diethoxyaniline [14], salicylamide [15], thiocyanates [16-18], sodium diethyldithiocarbamate [19], and many others. To this category belong, in addition, the carefully studied reaction with H_2O_2 [20], which has been recommended for the photometric determination of uranium [21, 22], and the reaction with $K_4Fe(CN)_6$ [23-25]. Photometric methods of determination which are based on the chromophoric effect have also been described for quadrivalent uranium [26].

Color reactions which are based on the chromophoric effect of elements are of relatively low sensitivity, for reasons which have been considered in detail elsewhere [27]. Color reactions with colored organic reagents are more sensitive. In such reactions, the color changes are related to changes in the ionic state of the colored reagents [28]. Since the inherent color of the reagents themselves is very intense, color reactions of this type are very sensitive. A number of such color reactions for uranium have been described in the literature: they include reactions with: quinalizarin [29], alizarin S [30], curcumin [31], quercetin and quercetrin [32], anthrazo [33], 4-amino-4-hydroxy-3'-carboxyazobenzene-2-sulfonic acid [6], 4-amino-3',4'-dihydroxyazobenzene-2-sulfonic acid [6], 4-amino-2-arsonic acid <1-azo-1> -2-hydroxynaphthalene-3,6-disulfonic acid [6], etc.



Arsenazo
(Uranon I)

To this latter group of reagents belongs the reagent arsenazo which has been described previously ("Uranon I"; benzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid); this reagent gives highly sensitive, and very contrasting color reactions, with both sexivalent [34], and quadrivalent [35] uranium. Arsenazo has also been recommended for color reactions with, and for the photometric determination of the rare earths [36], zirconium [37], thorium [34, 35, 38], aluminum [39], beryllium [40], and quadrivalent vanadium [41].

The present article contains a description of a color reaction for uranium (U^{VI} and U^{IV}) with arsenazo.*

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* The reaction was developed by the author in 1944.

The quantitative photometric determination of uranium by means of this reagent will be described later. A description of the synthesis of the reagent has been described previously [36].

Arsenazo (the sodium salt) is a dark brown crystalline powder which is readily soluble in water to give solutions of a red-rose color. The color does not change on acidification but changes to raspberry when its solution is made alkaline. Strong oxidizing agents (elemental chlorine and bromine, permanganate, hypochlorite) and reducing agents (Sn^{II}, Ti^{III}, $Na_2S_2O_4$) decolorize and break down the reagent. H_2O_2 does not affect the reagent in the cold.

Arsenazo gives color reactions – violet colors of different shades – with a number of elements [36, 40]. The effect of pH on the development of the color reactions of different elements is found to be in complete agreement with the general rules: the more readily does a given ion hydrolyze, the lower the pH of the solution in which arsenazo gives a color reaction [42, 43]. In accordance with this rule, U^{IV} like Th, gives a color reaction (blue-violet color) in a mineral acid medium, while U^{VI} (blue or light blue), like the rare earths and Be, only gives a color in a very weak acid medium, at pH 4.5-5.5.

Although arsenazo gives color reactions with many other elements apart from uranium, by carrying out the reaction under certain conditions, uranium can be detected quite reliably. A check reaction with H_2O_2 guarantees correct results even when deviations are made from the procedure that should be followed.

Detection of sexivalent uranium in pure solutions and in the presence of elements which do not react with arsenazo (K, Na, NH_4, Ca, Sr, Ba, Mg, Mn) is carried out as follows: to 1 ml of weakly acid or neutral test solution is added one drop of 3 N HCl and one to two drops of 0.02-0.05% aqueous arsenazo solution. A rose color indicates the absence of Th, U^{IV}, Zr, Ti, and Fe^{III}; three to four drops of a 25% solution of urotropine is then added. When U^{VI} is present a pure blue or violet color appears; when excess reagent is added, the color immediately changes to the original rose color of the reagent after addition of a drop of H_2O_2. The limit of identification is 0.2γ of U^{VI}; the limiting dilution is $1:5\cdot10^6$.

The blue color which develops in the presence of insufficient reagent is characteristic of sexivalent uranium alone and is suitable for providing convincing proof of its presence, since none of the other elements give a blue or pale blue color. Violet colors of different shades may develop in the presence of Th, U^{IV}, TR, V^{IV}, Al, Fe^{III}, Zr, Ti, Cu, Be, Cr, Ga, and Pd as well, but these colors (apart from those of U^{IV} and V^{IV}), after addition of H_2O_2, do not change immediately. The colors developed in the presence of U^{IV} and V^{IV} disappear immediately on addition of H_2O_2; nevertheless, these elements, even in the presence of insufficient reagent, only form violet colors and not the blue color formed by U^{VI}.

Fluorides, phosphates, arsenates, vanadates and H_2O_2, when present in amounts which are five to ten times that of the uranium present (in terms of U, F, P, As, V) and large amounts of sulfates, suppress the reaction considerably. Complexon III, salicylates, and sulfosalicylates exhibit only a weak effect.

When the reaction is carried out as a spot test, it is best to use filter paper which has been soaked with a 0.2% aqueous solution of arsenazo and dried. It is useful to have a capillary with a very fine diameter of about 0.2 mm at its tip.

A drop of the weakly acid test solution is evaporated on the lid of a crucible, and the residue dissolved in a micro drop of urotropine (ten drops of 25% urotropine + two drops of 3 N HCl) and the solution obtained taken up in the capillary. By touching the reagent filter paper with the tip of the capillary, some of the test solution is expressed.

When uranium is present a blue spot develops; this disappears on moistening with dilute H_2O_2.

The limit of identification is 0.05γ of U in a micro drop of 0.005 ml at a dilution of $1:1\cdot10^5$.

Detection of quadrivalent uranium in the presence of rare earths, V^V, Th, V^{IV}, Al, Fe^{II}, Be, and other elements is carried out as follows. By addition of HCl or CH_3COONa, an acidity of 0.02-0.05 N is created in the test solution; this is assessed by comparison with the color of methyl violet paper,* which has been moistened with 0.02 and 0.05 N HCl. To 1 ml of a solution prepared in this way is added a drop of 0.01-0.05% arsenazo solution. The development of a violet color which slowly changes to a rose color on addition of a drop of H_2O_2

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*This can be prepared by soaking filter paper with a dilute solution of the usual "chemical" (violet) ink.

indicates the presence of U^{IV}.

The limit of identification is 1-2 γ of U^{IV}.

Detection of U^{IV} is possible in the presence of a thousand times its amount of U^{VI}, V^{IV}, the rare earths and Be, and in the presence of Al and the divalent cations (Fe^{II}, Cu, Mn, Mg, etc.). In the presence of Fe^{II} the check reaction with H_2O_2 is of little use. Th, Zr, Ti, Fe^{III}, give colors which do not change immediately on addition of H_2O_2. Those anions which complicate detection of U^{VI} interfere, as well as tungstates and molybdates.

Detection of uranium (U^{VI}) in the presence of elements which react with arsenazo. By using selective masking, uranium can be detected in individual cases even in the presence of elements which react with arsenazo. The rare earths interact with arsenazo after complexing of any uranium which is present. Accordingly, since the colors formed by U^{VI} and the rare earths differ, on addition of arsenazo in small portions to a solution containing urotropine, it is possible to detect uranium in the presence of the rare earths at ratios of U^{VI} : rare earths = 1 : 1000. Comparison with a control test containing the rare earths alone is necessary.

Trivalent iron can be converted into Fe^{II} by the action of $Na_2S_2O_3$, ascorbic acid, or other reducing agents; uranium can then be detected at ratios of U^{VI} : Fe = 1 : 300 and higher. Urotropine should be added after addition of $Na_2S_2O_3$. Under the experimental conditions used, a large amount of Fe^{II} can lead to decomposition of the reagent.

Fluorides complex aluminum to a greater extent than U^{VI}. By adding fluoride in an amount which is only sufficient to mask aluminum, uranium can be detected in the presence of the latter. The test solution which has been treated with urotropine, and which weakly colors arsenazo, is split up into two separate beakers. To one is added a few drops of H_2O_2 and then to both beakers is added dropwise, at the same time and in equal amounts, a saturated solution of Na_2SiF_6 or a 0.5% NaF solution; the latter is inferior to Na_2SiF_6.

When no uranium is present, the color in both beakers changes to the same extent, the change being a gradual one from violet to rose. When uranium is present, the color of the solution to which H_2O_2 has not been added becomes more and more blue, becoming a pure blue if not too much aluminum is present, while the contents of the beaker containing the solution to which H_2O_2 has been added almost acquires the color of the reagent.

Detection of uranium is still possible at a ratio of U : Al = 1 : 250. When the amount of aluminum is twenty times that of uranium, a blue color can still be observed. In the presence of only three to four times its amount of aluminum, uranium can be detected directly.

Thorium and zirconium in amounts not more than ten times that of the U^{VI} can be masked by means of fluorides in the same way as aluminum. Copper can be masked by addition of $Na_2S_2O_3$.

Beryllium is complexed by addition of salicylates. 0.1 ml of a 10% solution of ammonium salicylate complexes 160γ Be, thereby permitting detection of 20γ of U in solution; this corresponds to a ratio of U : Be = = 1 : 8.

For the detection of sexivalent uranium in the presence of interfering phosphates or arsenates, the latter can be conveniently separated by means of stannic acid whereby, at the same time, the readily hydrolyzable ions Zr, Ti, Th, U^{IV}, Fe^{III}, Nb, and Ta can be removed. Such a separation is readily carried out by using "stannic chloride" (an approximately 60% aqueous solution of $SnCl_4$). On addition of a few drops of this "stannic chloride" to 0.02-0.03 N hydrochloric acid test solution, with subsequent heating, metastannic acid separates out and the latter traps the phosphates and arsenates and the elements whose cations hydrolyze readily. When the acidity is not less than that indicated, uranium (U^{VI}) remains quantitatively in solution together with aluminum, the rare earths, beryllium, and all the elements whose cations hydrolyze with difficulty. Work should be carried out in very dilute solutions. For facilitating coagulation of the stannic acid, particularly in the presence of iron, whose hydroxide forms a stable colloidal system with the hydrosol of metastannic acid [44], it is useful to add 3-5% NH_4NO_3. When separation with metastannic acid has been carried out successfully, the acid filtrate does not give a color reaction with arsenazo and does not become turbid on addition of urotropine.

Detection of uranium in minerals and rocks. When the uranium content is high – of the order of several percent – uranium can be detected, in several instances, without its preliminary separation from other elements. For the study of uranium minerals, a small particle of rock which is hardly visible is sufficient.

A few milligrams of the mineral which has been finely ground to a powder is heated in a test tube with two to three drops of a mixture of HCl and HNO_3 (3 : 1)*; 5 ml of water is added, and a very small piece of Congo Red paper placed in the solution; a drop of a saturated solution of $Na_2S_2O_3$ is then added. When the violet color (from Fe^{III} and $Na_2S_2O_3$) has disappeared, a 25% solution of urotropine is added dropwise until the Congo Red paper has turned red; two to three drops of urotropine are then added in excess. A 0.01-0.05% solution of arsenazo is next added to the solution. When uranium is present, a blue color appears, which slowly changes to a rose color on addition of H_2O_2. When iron is present, a brown precipitate of ferric hydroxide appears at this stage.

When the uranium content is low, 0.5-1 g of finely ground material is heated in a test tube with 1-2 ml of a mixture of HCl and HNO_3 (1 : 3). The solution is washed into a flask, and, without filtering, its volume is made up to about 100 ml, a piece of Congo Red paper is introduced into the flask, and $NaHCO_3$ solution added until the Congo paper is violet; 10-20 drops of the commercial aqueous 60% $SnCl_4$ solution is then added and the solution heated to the boil; after the precipitate has coagulated it is filtered off. Another piece of Congo paper is introduced into the filtrate, and 25% urotropine solution added until the indicator paper is red, 0.5 ml of urotropine solution is added in excess, arsenazo reagent is added and the solution divided into two. To one half is added a few drops of H_2O_2, after which a saturated solution of Na_2SiF_6 or a 0.5% solution of NaF is added to both halves dropwise, in equal amounts, and at the same time with thorough agitation.

When uranium is present, the contents of the beaker to which H_2O_2 has been added acquires an almost rose color, while the half to which no H_2O_2 has been added becomes violet.

Samples containing 0.005% uranium still give a clear-cut reaction for uranium, but with higher contents of aluminum, the reaction is not so distinct.

For detection of quadrivalent aluminum, 2-5 mg of finely ground mineral is placed in a very narrow test tube, and one drop (about 0.03 ml) of 6 N HCl is added; the mixture is carefully heated, care being taken to avoid evaporation of the drop. 2 ml of water is added and the solution heated to the boil for a further minute, it is then cooled and a drop of 0.01-0.05% solution of arsenazo added. The appearance of a violet color which changes immediately to rose on addition of a drop of H_2O_2 testifies to the presence of quadrivalent uranium.

SUMMARY

Arsenazo reagent (benzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid) dissolves in water to give solutions of a red-rose color; the latter, in the presence of uranium, changes to blue (sexivalent, pH about 4.5-5.5) or violet (quadrivalent, mineral acid media). U^{VI} is detected by addition to the acid test solution of reagent and urotropine. The limiting dilution for uranium is $1 : 5 \cdot 10^6$. On addition of H_2O_2, the color immediately changes to rose (check reaction). By using NaF, $Na_2S_2O_3$, and salicylates for masking, it is possible to detect U^{VI} in the presence of the rare earths, Fe, Al, Th, Zr, Cu and Be. Quadrivalent uranium in mineral acid media can be detected directly in the presence of large amounts of U^{VI}, the rare earths, V^{IV}, Be, Al, Fe^{III}, Cu, Mg, and a number of other elements. Cations (Fe^{III}, Zr, Ti, Th) and anions (phosphates, arsenates) which interfere with the reaction can be removed by coprecipitation with metastannic acid, which separates out during hydrolysis of added $SnCl_4$ solution. Qualitative reactions for U^{VI} and U^{IV} are described, together with procedures for detecting U^{VI} and U^{IV} in minerals.

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* Silicates are fused in the loop of a platinum wire with soda, the melt is then treated, and acidified, and the procedure outlined for acid decomposition subsequently followed.

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POLAROGRAPHIC DETERMINATION ON SOLID ELECTRODES OF OZONE AND CHLORINE IN THE AIR OF INDUSTRIAL CONCERNS

COMMUNICATION II*

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Determination of Ozone in Air

The limiting permissible ozone concentration of the air, according to Lazarev and Astrakhatsev's results [1], is 0.0001 mg/liter. Of the chemical methods for determining ozone in air, worthy of mention are those based on oxidation of $NaNO_2$ [2], and of potassium iodide with subsequent titrimetric determination of the iodine liberated.

An electrochemical method [3] based on the polarographic determination of iodine liberated during the interaction of ozone with potassium iodide has been developed. The luminescence method of determining ozone in air [4] is not applicable when other oxidizing agents are present in the air.

The problem confronting us was to develop a method which would permit determination of small concentrations of ozone in small volumes of air, using the solid rotating electrode technique. Solid electrodes have been used in polarography by a number of workers [5-9]. The basis of the method was oxidation of potassium iodide with ozone according to the following equation:

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^-. \qquad (1)$$

The amount of iodide ions remaining after oxidation was determined polarographically on a rotating solid anode, in a supporting electrolyte of 0.1 N chloride or hydrochloric acid.

The anode was a smooth platinum wire 1 mm in diameter and 17 mm long twisted into a spiral. The cathode was a large calomel electrode. Contact was realized through an agar bridge. A synchronous motor rotated the electrode at the rate of 750 rpm.

In a supporting electrolyte of 0.1 N HCl, at molar concentrations of potassium iodide ranging from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ moles/liter, the strength of the diffusion current is proportional to the concentration of the iodide ions.

The half-wave potential for potassium iodide is equal to +0.55 volt (with respect to the saturated calomel electrode). Oxidation of potassium iodide on a platinum anode gives normal polarographic waves with clearly defined limiting currents (Figure 1). Complete reproducibility of the current strength and the polarograms is observed. The straight line calibration curve is shown in Figure 1.

Quantitative Determination of Ozone in Air

Ozone was prepared in a gas chamber with a capacity of 0.9 m^3 by means of a PRK-2 ultraviolet lamp.

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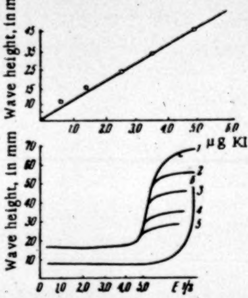

Fig. 1. Polarograms and calibration curve for potassium iodide in the concentration range 0.5-5γ KI: 1) 3.75γ; 2) 3γ; 3) 2.2γ; 4) 1.5γ; 5) 1.0γ; 6) 0.

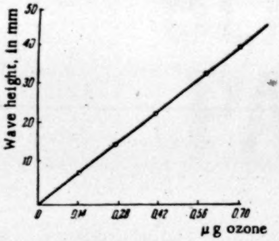

Fig. 2. Calibration curve for ozone.

TABLE 1

Results of Determinations of Ozone in Air as a Function of the Time of Standing of the Test Sample in the Bottle With Test Air

Time from moment of sampling to analysis, in minutes	Ozone found in 1 liter of air, in γ
30	0.29
60	0.33
90	0.26
180	0.27
240	0.33
300	0.27
380	0.23

Air samples were taken from the chamber into 5-liter darkened bottles, from which the air had been pumped out [10]. Before samples were taken, an absorption solution containing 10 γ of KI was introduced into the bottles. The sampled ozonized air was left for 1-1.5 hours in the dark. The walls of the bottle were moistened with the absorption solution. For analysis, a measured amount of the absorption solution from the bottle was transferred to a porcelain basin. The solution was evaporated to dryness on a water bath. The residue was dissolved in the basin in 0.5 ml water. The basin was rinsed with 1 ml of 0.1 N HCl, and the solution transferred to the electrolyzer and polarograms taken.

At the same time, a solution of KI containing 10γ KI was introduced into another basin; this solution was evaporated to dryness and the residue dissolved in 0.5 ml water; 1 ml of 0.1 N HCl was finally added, and the polarograms taken again.

The wave heights found in the two polarograms for sample and the KI solution, respectively, were subtracted from each other.

The amount of ozone in the sample was then established by means of the calibration curve (Figure 2).

The calibration curve for ozone was derived from the curve drawn for potassium iodide, after appropriate conversion of the amount of potassium iodide to ozone by means of Equation (1).

Blanks were carried out at the same time as the quantitative determination of the ozone in the air of the chamber. For this purpose, before the ultraviolet lamp was switched on, a ventilator was introduced into the chamber and, after ventilation of the chamber, a sample of air was introduced into an evacuated bottle. The analysis was carried out as described above.

Thirty minutes (Table 1) was found to be sufficient for the reaction between the ozone and the solution of potassium iodide in the bottle to go to completion at ozone concentrations of 0.2-0.3 γ/liter.

Table 2 contains the results for determination of ozone in the air of the chamber.

It was found that under the experimental conditions used, nitrogen dioxide does not interfere with determination of ozone in air; nitric acid was detected in amounts of 4.2-5.7 γ/liter in the air. We are of the opinion that the nitrogen dioxide is oxidized by ozone into nitric acid.

The method described for the determination of ozone in air has been used for developing health precautions in industrial establishments [11].

Determination of Chlorine on Solid Electrodes

The limiting permissible concentration of chlorine in air is 0.001 γ/ml.

Our problem was to develop a sensitive and accurate method — no less accurate than existing methods — requiring small volumes of test air of the order of 0.5-1 liter.

The basis of our method of determining chlorine was oxi-

TABLE 2

Determination of Ozone in the Air of the Chamber

Conditions under which sample was taken	Ozone found in 1 liter of air, in γ
10 minutes after PRK-2 lamp had been switched on, without ventilation	0.47
15 minutes after lamp was switched on	0.46
20 minutes " "	0.46
30 minutes " "	0.40
55 minutes " "	0.26

dation of potassium iodide by chlorine according to the following reaction: $Cl_2 + 2I^- = I_2 + 2Cl^-$.

The potassium iodide remaining after the reaction was determined on a solid rotating electrode [12].

The effect of the supporting electrolyte on the diffusion current of KI is evident from Table 3.

Complex waves are observed in sulfuric acid media. In nitric acid media and also in sulfate and nitrate solutions, the waves for oxidation of iodine are poorly defined and cannot be used for the quantitative determination of KI.

The nature of the current-voltage curves are shown in Figure 3.

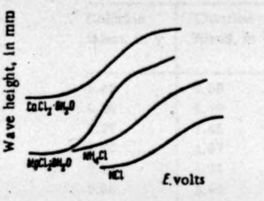

Fig. 3. Polarograms of KI solutions as a function of electrolyte composition.

It is evident from the results obtained that chlorides can be used successfully as the supporting electrolyte for the quantitative determination of I^-. A 0.5 N solution of $MgCl_2 \cdot 6H_2O$ is preferred since the height of the diffusion wave for KI in this supporting electrolyte is higher than those obtained in other chlorides.

Polarograms for I^- in a supporting electrolyte of 0.5 N $MgCl_2 \cdot 6H_2O$ are shown in Figure 4, as well as the calibration curve for chlorine.

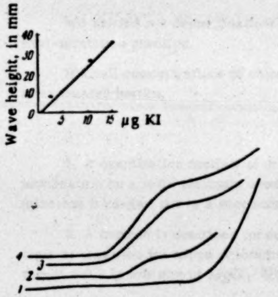

Fig. 4. Polarograms for iodine ions in a supporting electrolyte of 0.5 N $MgCl_2 \cdot 6H_2O$: 1) supporting electrolyte – 0.5 N $MgCl_2 \cdot 6H_2O$; 2) 3 γ KI; 3) 10 γ KI; 4) 15 γ KI.

For the quantitative determination of chlorine by the polarographic method, chlorine water was prepared by saturation of twice distilled water with pure, gaseous chlorine. By appropriate dilution of the chlorine water thus prepared, solutions were prepared with chlorine concentrations of the order of $1.2 \cdot 10^{-4}$ M/liter. The chlorine concentration of the chlorine water was determined iodometrically before each test. For analysis, solution of chlorine water was added to a KI solution of known concentration. The solution was evaporated to dryness. The residue was dissolved in water, and the solution obtained transferred to an electrolyzer; polarograms were then taken in a supporting electrolyte of 0.5 M $MgCl_2 \cdot 6H_2O$.

At the same time polarograms were taken for a solution of KI taken in the same amount as that for analyzing the chlorine.

TABLE 3

Effect of the Supporting Electrolyte on the Diffusion Current of KI

Supporting electrolyte, 0.1 M solution	Wave height, in mm	KI concentration, in γ
KCl	14	10
$MgCl_2 \cdot 6H_2O$	27	10
NH_4Cl	23	10
$BaCl_2$	27	10
$CaCl_2$	20	10
HCl	20	10

TABLE 4

Polarographic Determination of Chlorine on a Solid Rotating Electrode

Chlorine taken, in γ	Chlorine found, in γ	Amount determined, in %	Chlorine taken, in γ	Chlorine found, in γ	Amount determined, in %
0.42	0.58	138	3.4	2.95	86
0.85	0.70	82	4.25	3.35	78
1.27	1.45	113	4.40	3.85	87
1.70	1.57	92	8.5	6.37	75
2.12	1.95	92	10.5	8.55	81
2.55	1.95	76	17.0	13.3	78

The chlorine concentration was determined from the differences in height for the KI solution before and after addition of chlorine.

We carried out determinations of chlorine over the wide range of concentrations which are met in industrial-sanitation practice.

If small concentrations of chlorine are to be determined, sampling could be carried out by taking the air in evacuated bottles.

SUMMARY

1. A quantitative method of determining ozone in air is described which is based on the polarographic determination on a solid platinum anode of iodide ions which have not reacted with the oxidizing agent. Determination is carried out in a supporting electrolyte of 0.1 M HCl.

2. A method is described for determination of chlorine in liquids and air, which is based on the same principle as that used for ozone determination. The most satisfactory supporting electrolyte for chlorine determination is a 0.1 M solution of $MgCl_2 \cdot 6H_2O$. 0.1 M HCl can also be used as the supporting electrolyte.

3. The sensitivity of the method for ozone is 0.1γ, while for chlorine it is 0.5γ in 1.5 ml of liquid.

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NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF NITROGEN AND HALOGENS AND ALSO FOR THE DETERMINATION OF NITROGEN, SULFUR AND HALOGENS ON ONE ALIQUOT OF ORGANIC MATERIAL

COMMUNICATION IV

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In previous communications [1, 2] we have indicated that on heating nitrogen-, sulfur- and halogen-containing organic materials with powdered magnesium metal to temperatures of 550-650°, magnesium nitride, sulfide and halides are formed respectively.

The present article contains a description of a technique which permits simultaneous determination of two and three elements on one aliquot of organic material; in addition, the possibility is demonstrated of simultaneously determining sulfur and nitrogen in various types of coal.

Instead of hydrogen, which we used earlier for driving the air from the reaction tube, diethyl ether can be used. This simplifies the method considerably.*

EXPERIMENTAL

Simultaneous Determination of Nitrogen and Halogens on One Aliquot of Organic Material

A sample of the test organic material (0.05-0.10 g) is placed in a glass test tube 10-15 cm long and 1-1.5 cm in diameter; it is mixed with a small amount of magnesium and powdered magnesium metal sprinkled over it, until the tube is approximately half full. 0.5-0.7 ml of ether is introduced by means of a pipet into the test tube, and the test tube then placed in a beaker containing distilled water at a temperature of 40-50°. The test tube is completely filled with powdered magnesium and a further 0.5-0.7 ml of ether introduced; the tube is finally sealed with a stopper fitted with a rubber tube for leading away gases. The free end of this tube is led under a cylinder filled with water. The test tube is fitted into an electric oven, or is heated with a gas burner (Communication 1). After heating, the cooled, partially deformed test tube and its contents are ground up in a porcelain mortar and transferred quantitatively into a distillation flask for distilling off the ammonia. The air is displaced from the flask with carbon dioxide and the reaction mass treated with 25-35 ml of 40% sulfuric acid until the magnesium has completely dissolved. The solution is made alkaline with 15-20 ml of 50% potassium hydroxide, and the ammonia distilled off. It is best to use 0.1 N potassium biiodate for absorbing the ammonia [3]. Nitrogen is thereby determined iodometrically. When the ammonia has been removed (about one-third of the contents of the flask is distilled), the absorption flask is disconnected, and 10 ml of 10% potassium iodide added to it; after standing for five minutes the iodine liberated is titrated with 0.1 N sodium thiosulfate.

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*Replacement of hydrogen by ether was tried out at the suggestion of A.P. Terent'ev, to whom we should like to express our thanks at this juncture.

TABLE 1

Expt. No.	Test material and its formula	Amt test material, in g	0.1 N $KH(IO_3)_2$ used, ml	% Nitrogen			0.1 N $AgNO_3$ used up, ml	% Halogen		
				calc.	found	difference		calc.	found	difference
1	Tribromoaniline	0.0402	1.20	4.25	4.18	−0.07	3.65	72.68	72.55	−0.13
	$C_6H_4Br_3N$	0.0492	1.40	4.25	3.98	−0.27	4.48	72.68	72.74	+0.06
2	Chloroaniline C_6H_6NCl	0.0487	3.70	10.98	10.65	−0.33	3.78	27.78	27.52	−0.26
		0.1010	7.80	10.98	10.82	−0.16	7.85	27.78	27.55	−0.23
3	Quinine hydrochloride	0.0507	2.60	7.06	7.18	+0.12	1.30	8.94	9.09	+0.15
	$C_{20}H_{24}N_2O_2HCl \cdot 2H_2O$	0.0896	4.40	7.06	6.87	−0.19	2.20	8.94	8.71	−0.22
4	Bromoisovalerylurea									
	$C_{13}H_{11}O_2N_2Br$	0.0462	4.20	12.73	12.56	−0.17	2.07	35.86	35.78	−0.05
		0.1028	9.95	12.73	12.48	−0.25	4.60	35.86	35.81	−0.10
5	Piperine $C_{17}H_{19}O_3N$	0.0519	1.80	4.90	4.86	−0.05				
	Tetrachlorophthalic acid $C_8H_2O_4Cl \cdot 1/2\ H_2O$	0.0490					6.30	45.32	45.58	+0.26
	Total aliquot	0.1009								
6	Piperine $C_{17}H_{19}O_3N$	0.0498	1.82	4.90	5.00	+0.10				
	Tetrachlorophthalic acid $C_8H_2O_4Cl_4 \cdot 1/2H_2O$	0.0488					6.25	45.32	45.49	+0.17
	Total aliquot	0.0986								
7	Nitroanisole $C_7H_7O_3N$	0.0257	1.63	9.15	8.88	−0.23				
	Dibromobenzene $C_6H_4Br_2$	0.0275					2.33	67.70	67.71	+0.01
	Total aliquot	0.0532								
8	Nitroanisole $C_7H_7NO_3$	0.0247	1.57	9.15	8.90	−0.25				
	Hexachloroethane C	0.0263					6.67	89.85	89.92	+0.07
	Total aliquot	0.0510								
9	Nitroanisole $C_7H_7NO_3$	0.0251	1.60	9.15	8.93	−0.22				
	Tribromophenol	0.0248					2.25	72.43	72.50	+0.07
	Total aliquot	0.0499								
10	Nitroanisole $C_7H_7NO_3$	0.0242	1.54	9.15	8.91	−0.24				
	Tetrachlorophthalic acid $C_8H_2O_4Cl_4 \cdot 1/2H_2O$	0.0271					3.45	45.32	45.13	−0.19
	Total aliquot	0.0513								
11	Oxanilide $C_{14}H_{12}O_2N_2$	0.0249	2.10	11.66	11.81	+0.15				
	Tetrachlorophthalic acid $C_{82}O_4Cl_4 \cdot 1/2\ H_2O$	0.0255					3.25	45.32	45.19	−0.13
	Total aliquot	0.0504								

Note: In experiments Nos. 5-11, synthetic mixtures of materials containing nitrogen and halogens were analyzed.

TABLE 2

Expt. No.	Test material and its formula	Amount test material (g)	0.1 N I_2 solution used up, in ml	% Sulfur			0.1 N $KH(IO_3)_2$ used up, in ml	% Nitrogen			0.1 N $AgNO_3$ used up, in ml	% Halogen		
				calc.	found	difference		calc.	found	difference		calc.	found	difference
1	Sulfosalicylic acid $C_7H_6SO_6 \cdot 2H_2O$	0.0246	1.90	12.61	12.38	−0.23								
	p-Bromonitrobenzene $C_6H_4BrNO_2$	0.0304					1.50	6.94	6.91	−0.03	1.50	39.55	39.43	−0.12
	Total aliquot	0.0550												
2	Sulfosalicylic acid $C_7H_6SO_6 \cdot 2H_2O$	0.0248	1.90	12.61	12.28	−0.33								
	p-Bromonitrobenzene $C_6H_4BrNO_2$	0.0384					1.84	6.94	6.71	−0.23	1.90	39.55	39.54	−0.01
	Total aliquot	0.0632												
3	Sulfosalicylic acid $C_7H_6SO_6 \cdot 2H_2O$	0.0262	2.04	12.61	12.48	−0.13								
	Chloroaniline C_6H_6NCl	0.0302					2.34	10.98	10.85	−0.13	2.35	27.78	27.59	−0.13
	Total aliquot	0.0564												
4	Sulfosalicylic acid $C_7H_6SO_6 \cdot 2H_2O$	0.0222	1.75	12.61	12.63	+0.02								
	Chloroaniline C_6H_6NCl	0.0284					2.20	10.98	10.85	−0.13	2.25	27.78	28.09	+0.31
	Total aliquot	0.0506												
5	Naphthionic acid $C_{10}H_9NSO_3 \cdot 1/2\ H_2O$	0.0304	2.00	13.81	13.71	−0.10	1.30	6.03	5.98	−0.05				
	Iodoform CHI_3	0.0300									2.28	96.69	96.45	−0.24
	Total aliquot	0.0604												
6	Sodium alizarin sulfonate $C_{14}H_7O_7SNa \cdot H_2O$	0.0263	1.56	9.37	9.51	+0.14								
	p-Bromonitrobenzene $C_6H_4BrNO_2$	0.0340					1.61	6.94	6.63	−0.31	1.67	39.55	39.26	−0.29
	Total aliquot	0.0603												
7	Bis-(1,1-dimethylpentene-3-OH-sulfide) $C_{14}H_{26}O_2S$	0.0243	1.95	12.60	12.84	+0.24								
	Tribromoaniline $C_6H_4Br_3N$	0.0293					0.90	4.12	4.30	+0.18	2.68	72.68	73.09	+0.32
	Total aliquot	0.0536												
8	Sodium alizarin sulfonate $C_{14}H_7O_7SNa \cdot H_2O$	0.0224	1.30	9.37	9.30	−0.07								
	Chloroaniline C_6H_6NCl	0.0305					2.34	10.98	10.74	−0.24	2.40	27.78	27.89	+0.11

Note: Synthetic mixtures of materials containing sulfur, nitrogen, and halogens were analyzed.

TABLE 3

Expt. No.	Designation of test coal	Amt coal taken (in g) (on dry material)	% C^f	% H^f	% W^{as}	% A^{as}	% V^f	0.1 N I_2 solution used up, in ml	% Sulfur found VTI*	% Sulfur found NKI**	% Sulfur difference	0.1 N $KH(IO_3)_2$ used up, in ml	% Nitrogen found VTI*	% Nitrogen found NKI**	% Nitrogen difference
1	Coal AN-9739	0.1007	90.6	3.8	1.11	13.73	8.48	0.96	1,39	1.53	+0.14	0.86	1.24	1.19	−0.05
		0.0924	90.6	3.8	1.11	13.73	8.48	0.965	1.39	1.65	+0.27	0.67	1.24	1.01	−0.29
2	Coal AN-10100	0.1057	89.8	3.6	1.03	9.31	—	2.55	4.01	3.89	−0.12	1.06	1.39	1.40	+0.01
		0.0590	89.8	3.6	1.03	9.31	—	1.49	4.01	4.05	+0.04	0.67	1.39	1.59	+0.20
3	Coal 9986	0.1030	88.5	4.4	0.77	16.06	—	1.59	2.34	2.47	+0.13	1.15	1.38	1.56	+0.18
		0.0786	88.5	4.4	0.77	16.06	—	1.10	2.34	2.24	−0.10	0.86	1.38	1.53	+0.12
4	Coal AN-10050	0.0695	89.8	3.9	1.05	18.67	—	1.01	2.28	2.33	+0.05	0.77	1.40	1.55	+0.15
		0.0831	89.8	3.9	1.05	18.67	—	1.10	2.28	2.12	−0.16	0.68	1.40	1.15	−0,25
5	Coal AN-114	0.0656	77	—	2.90	22.90	45.2	0.52	1.12	1.27	+0.15	0.63	1.56	1.34	−0,22
		0.0930	77	—	2.90	22.90	45.2	0.81	1.12	1.39	+0.27	0.92	1.56	1.38	−0,18
6	Coal AN-8	0.0763	77	3.6	6.76	17.85	3.08	0.28	0.31	0.51	+0.20	1.01	2,14	1.86	−0.28
		0.0779	77	3.6	6.76	17.85	3,08	0.28	0.31	0.57	+0.26	1.06	2.14	1.98	−0.25
7	Coal AN-117	0.1012	86.6	—	0.61	25.48	25.6	1.06	1.60	1.68	+0.08	1.16	1.70	1.61	+0.09
		0.1220	86.6	—	0.61	25.48	25,6	1.35	1.60	1.77	+0.17	1.30	1.70	1.50	−0.20
8	Coal AN-96	0.1093	83.4	5.4	1.04	28.66	32.52	1.80	2.53	2.64	+0.11	1,20	1.61	1.53	−0.09
		0.1019	83.4	5.4	1.04	28.66	32.52	1.49	2.53	2.34	−0.19	1.02	1.61	1.40	−0.21

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*According to the results of VTI (The Dzerzhinskii All-Union Heat Technical Institute).

**According to the results of NKI (The S.O. Makarov Nikolaev Shipbuilding Institute): C^f is the percentage carbon on the fuel; H^f is the percentage of hydrogen on the fuel; W^{as} is the percentage of water in the analytical sample; A^{ds} the percentage ash on the dry sample; V^f is the percentage of volatile material on the fuel.

To the residue in the flask used for distillation is added 40% sulfuric acid until the precipitate of $Mg(OH)_2$ has dissolved; the solution is filtered free from carbon and the pieces of glass from the test tube. The filter is carefully washed with distilled water and the wash liquors combined with the filtrate. The halogen content of the filtrate is then determined argentimetrically.

The results obtained are given in Table 1.

Simultaneous Determination of Nitrogen, Sulfur and Halogens on One Aliquot of Organic Test Material

A sample of the organic test material is placed in a glass test tube and powdered magnesium added; the air is expelled by means of ether; the test tube and its contents are heated to 550-650° over a period of 20-30 minutes (as described above). When heating is finished, the cooled test tube is ground up in a porcelain mortar, and the material transferred quantitatively into a distillation flask for driving off the hydrogen sulfide [2]. The air is expelled from the apparatus by means of carbon dioxide, and the reaction mass treated with 25-35 ml of 40% sulfuric acid until all the magnesium has dissolved; the hydrogen sulfide is driven off and the sulfur determined iodometrically (see above). The flask used for distillation and containing the residue left after removal of hydrogen sulfide is then connected to a receiver for absorbing ammonia; the receiver contains 20 ml of 0.1N potassium biiodate. The acid solution in the distillation flask is made alkaline with 15-20 ml of 50% potassium hydroxide and, having driven off the ammonia, the nitrogen content of the original sample is determined iodometrically. After the hydrogen sulfide and ammonia have been removed, the contents of the flask are acidified with 40% sulfuric acid until all the $Mg(OH)_2$ has dissolved. The solid residues are filtered off and the filter carefully washed with distilled water; halogens are then determined in the combined filtrate and wash liquors.

The results obtained by this method are given in Table 2.

Table 3 contains the results obtained during analysis of various samples of industrial coal.

The method is fairly reliable and simple, and does not require any complicated apparatus and expensive materials; it should therefore find wide application in various laboratories.

SUMMARY

Quantitative methods are described for the simultaneous determination of nitrogen and halogens, as well as of nitrogen, sulfur, and halogens on one aliquot of an organic test material, coal for example.

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DETERMINATION OF NORMAL HYDROCARBONS IN PARAFFINS BY THE ADSORPTION ANALYSIS METHOD

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Determination of the normal-hydrocarbon content of commercial paraffins and ceresins is of considerable interest from the point of view of the industrial utilization of these materials. Thus, with increasing normal-hydrocarbon concentration of the paraffin to be oxidized, the efficiency of the latter increases and the composition of the distilled fatty acid improves considerably [1].

The techniques in current use for the quantitative separation of normal- and iso-hydrocarbons have serious drawbacks. The reaction of paraffin hydrocarbons with fuming sulfuric acid can, even under the best conditions, only be regarded as semiquantitative and cannot be used for the quantitative separation of normal- from iso-hydrocarbons [2, 3]. The classical nitration method of Konovalov [4], while permitting characterization of primary, secondary and tertiary carbon atoms, cannot be regarded as a strictly quantitative method either [5]. The method of determining iso-paraffins in a mixture with normal-paraffins by means of antimony pentachloride [2, 6-8] only permits determination of total hydrocarbons with a tertiary carbon atom, since antimony pentachloride reacts, not only with iso-paraffins, but also with naphthenic hydrocarbons.

The urea method of determining normal hydrocarbons has been finding wider application in analytical chemistry in recent years. It is known [9] that iso-hydrocarbons with strongly branched chains, and also cycloparaffins do not give penetration compounds with urea, since the cross section of the molecules of these compounds is considerably greater than the internal diameter of the elementary lattice cell of urea which is equal to 5A. Two variants of the urea method have been published. Hessier and Meinhardt [10] treat a solution of paraffin in carbon tetrachloride with a saturated solution of urea in methanol. The crystalline interaction product is then decomposed with water. Formation of the penetration compound is a reversible reaction and the final equilibrium state depends on a number of variables: temperature, concentration of the dissolved materials, nature of the solvent, ratio of solvent and activator (methanol, water, and other urea solvents are used as activators). It is difficult to take into account all these variables, accordingly, Hessler and Meinhardt have fixed these variables, and emphasize that even small deviations from their recommended procedure will lead to considerable errors of determination. Further, one must also bear in mind that hydrocarbons with weakly branched chains also penetrate into the urea lattice, the penetration being easier, the longer the hydrocarbon chain. This observation of Schlenk [11] has been confirmed by very recent work [12]. In general, both factors – dissociation of the urea complex and trapping of iso-compounds by the carbamide lattice – act in opposition on the final analytical results, but the extent of the mutual compensation of errors is not amenable to calculation.

Later, Hessler and Meinhardt, pursuing the aim of shifting the equilibrium toward formation of the penetration complex, made their method much more complicated by using a six-fold precipitation of normal-hydrocarbons with carbamide [13]. This technique involves a considerable increase in the amount of reagents necessary (1.4 liters of CCl_4, 1.4 liters of methanol and 420 g of urea are required for the analysis of 10 g of paraffin), while the time taken for one analysis becomes very great.

In the second variant proposed by Rosenberg, Genekh and Nikitina [14], the solution of test hydrocarbons is treated with solid urea and activator is added. The effect of dissociation of the complex and trapping of iso-compounds are not discussed in their article. From an experimental point of view, this second variant is incomparably simpler than that described in [10, 13].

The present article is devoted to further development of the determination of normal hydrocarbons by means of urea. Essentially, the work reduces to establishing an experimental basis for the assumption that the interaction of normal hydrocarbons with urea is an adsorption process, and to the development of a technique for the quantitative determination of normal hydrocarbons, based on the analysis of the adsorption isotherm.

EXPERIMENTAL

The interaction products of hydrocarbons with urea are not classical chemical compounds [15], not only because their formation does not conform to whole number stoichiometric ratios [11], but also because their energies of formation do not correspond in magnitude to Van-der-Waals' interaction forces. Actually, formation of the interaction products is accompanied by evolution of about 1.6 kilo calories per atom of carbon [16]. The formation energy of these complexes is scarcely twice the value of the heat effect, since their formation is accompanied not only by an increase but, more probably by a decrease in entropy, i.e., by an increase in order as compared with the original state of the system. In accordance with some ideas about the nature of this process outlined in [16], we suggest that interaction of urea with hydrocarbons is an adsorption process.

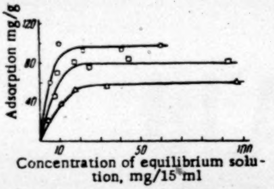

Fig. 1. Adsorption isotherms for hydrocarbon fractions: △) M = 338; □) M = 492; ○) M = 562.

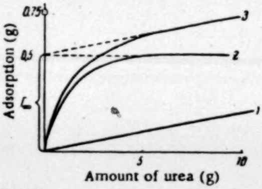

Fig. 2. Scheme for graphical extrapolation: 1) adsorption isotherm for iso-compounds; 2) adsorption isotherm for normal-hydrocarbons; 3) experimental isotherm; amount of paraffin in solution; amount of normal hydrocarbons in solution.

We have studied adsorption isotherms of narrow fractions of purified normal hydrocarbons on urea. The fractions were obtained by extractive crystallization from solutions of commercial paraffins and petroleum ether by means of urea. The molecular weight of the fractions was determined by measuring the dynamic viscosity at 55-80°. It is known that, at least for not too great temperature ranges, the viscosity is an exponential function of the absolute temperature [17, 18], i.e., the logarithm of the viscosity changes linearly with changes in the reciprocal of the absolute temperature:

$$\log\ \eta = \frac{B}{T} - A, \qquad (1)$$

where A and B are constants.

Mumford [19], having generalized the experimental results of many authors on the temperature relationship of the viscosity of liquid paraffin hydrocarbons, has shown that the constant B in Equation (1) is a linear function of the molecular weight.

From the slopes in Equation (1), and from the results given in [19], the mean molecular weights of the fractions were calculated.

Experiments on the study of the adsorption of these fractions were carried out at room temperature in 100 ml bottles with close fitting ground glass stoppers. The solvent used was benzene to which was added two percent by volume of methanol.* Chemically pure urea was ground up and sieved through a No. 25 sieve. 60 ml of solution and 1.2 g of urea were placed in each bottle. Shaking was carried out on a mechanical shaker for two hours. The paraffin concentration of the equilibrium solutions was determined by evaporating 10 ml of the solution. Some of the adsorption isotherms obtained are shown in Figure 1.

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*When activators are not added (alcohol, water) the paraffin fractions will not react with urea. It has been suggested [16] that the activators, which are urea solvents, form a pure adsorptive surface free from reaction inhibitors (sulfide and others). Preliminary tests showed that the solubility of urea in solutions containing 2% methanol lies outside the limits of the sensitivity of the experimental technique used in the work described in the present article.

The isotherms exhibit horizontal parts which correspond to limiting adsorption, and conform quite well to the Langmuir equation in the form

$$\frac{C}{\Gamma}=\frac{C}{\Gamma_{\infty}}+\frac{1}{\kappa\Gamma_{\infty}}, \tag{2}$$

where C is the equilibrium concentration, Γ is the adsorption in terms of grams per gram of urea, Γ_{∞} is the limiting adsorption, and k is a constant.

From the results we obtained, it follows that the values of the adsorption coefficients, and also of the limiting values of the adsorption, are functions of the molecular weight of the fractions. Consequently, analysis of adsorption isotherms can be used as the basis of a quantitative method of determining normal hydrocarbons.

The problem forming the subject of the present article – total determination of normal-hydrocarbons in commercial paraffins – can be solved as follows. Adsorption isotherms are drawn by adding to a series of solutions containing the same amount of test paraffin, increasing amounts of urea. When the test paraffin contains only normal hydrocarbons the adsorption isotherm terminates in a clearly defined horizontal part, corresponding to complete adsorption of normal hydrocarbons. If, on the other hand, the test paraffin contains iso-hydrocarbons with weakly branched chains, the isotherm terminates (on addition of the same amount of urea) in a part which slopes to the abscissa and not in a horizontal part.

Actually, in the latter case the experimentally drawn adsorption isotherm is the resultant of two isotherms: the adsorption isotherm for normal-hydrocarbons and the adsorption isotherm for iso-hydrocarbons. Since the value of the adsorption coefficient of iso-hydrocarbons is very small, the adsorption isotherm of these hydrocarbons will be much lower than the isotherms for the normal-hydrocarbons, and the horizontal parts on them will be reached only after addition of very large amounts of urea. In other words, the horizontal parts of both isotherms are so far removed from one another along the abscissa, that over the range where the adsorption isotherm for normal-hydrocarbons is complete, the adsorption isotherm for iso-hydrocarbons can be depicted without serious error by a straight line. The isotherms for both processes and also the resultant (i.e., the experimental) isotherm, obtained by combining the ordinates of both isotherms,are schematically shown in Figure 2.

From Figure 2 it is evident that the normal-hydrocarbon content of the test paraffin fraction is equal to the intercept on the ordinate, obtained by extrapolating the sloping part of the resultant isotherm onto the ordinate corresponding to zero addition of urea.* The difference between the amount actually taken for analysis and the amount of normal hydrocarbons found by graphical extrapolation is equal to the isoparaffin content of the aliquot taken.**

This technique was used for the determination of normal hydrocarbons in four samples of commercial paraffins.

Analyses were carried out on solutions in benzene, toluene and carbon tetrachloride.*** In most cases, the adsorption isotherms of the commercial paraffins were compared with the isotherms of the same paraffins freed from isoparaffins. The adsorption isotherms obtained are shown in Figures 3-5. The final analytical results are given in the table, which also contains results obtained by other techniques (mainly by the Hessler-Meinhardt method).

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*This technique is completely analogous to the widely used method of dividing the over-all swelling process of high polymers into two stages: the swelling process proper, and the secondary stage which is determined by destructive oxidation of the polymer [20].

**By "isoparaffins" in contrast to the term "hydrocarbons of iso structure" we, in accordance with the tradition established in the literature on petroleum chemistry [21], mean those paraffin fractions which are not composed of hydrocarbons with normal structure. Hydrocarbons with a cyclic structure belong to this class of iso-hydrocarbons in addition to the iso compounds.

***Samples for analysis of solutions in carbon tetrachloride were taken by means of a pipet with a filter plug at the tip.

DISCUSSION OF RESULTS

Of interest is the difference in the paths followed by the adsorption isotherms of the original and the purified paraffins. In the latter, the isotherms terminate in clearly defined horizontal sections corresponding to almost complete adsorption of the dissolved paraffin, while the adsorption isotherm of the original paraffins is always lower than that for the purified paraffins, and terminates in straight line sections sloping toward the abscissa, which characterize the difficulty of adsorption of iso-hydrocarbons.•

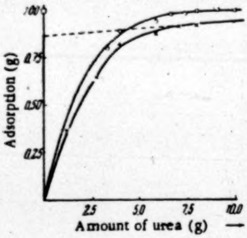

Fig. 3. Adsorption of paraffin No. 2 from benzene: O) purified paraffin; x) original paraffin; ☐) initial amount of paraffin in solution.

It is obvious from Figures 3-5 that the ordinates of the horizontal parts of the isotherms for the purified paraffins are approximately 1.5% less than the ordinates corresponding to the original aliquot. This difference is determined by errors in taking samples of solution for analysis and errors in converting the result of this analysis in terms of all the equilibrium solution on the one hand, and by errors which arise as a result of evaporation of solvent during shaking of the bottles (the stoppers, naturally, are not greased). The error which arises during graphical extrapolation of the sloping parts of the isotherms amounts to about 2%.

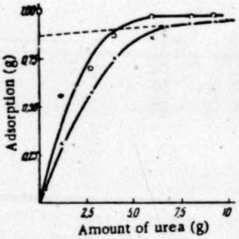

Fig. 4. Adsorption of paraffin No. 2 from toluene: x) original paraffin; O) purified paraffin; ☐) initial amount of paraffin in solution.

The content of normal hydrocarbons in the same sample of commercial material, as found by graphical extrapolation of the sloping section of the isotherm, is independent of the nature of the solvent. This conclusion is confirmed by the analytical results for paraffin No. 1 and particularly by those for No. 2, for which the adsorption isotherms were studied in three solvents: benzene, toluene, and carbon tetrachloride. These facts are convincing proof of the reliability of the technique suggested. The fact that the analytical results obtained for one sample in various solvents agree with one another, in most cases with an accuracy greater than 1.5%, is fully comprehensible since the sources of errors, mentioned above, are approximately the same for all solvents and accordingly would be excluded.••

It is clear from the table that the results of analysis of paraffins studied during the course of the work described in the present article, and carried out by the Hessler-Meinhardt method, are close to those obtained by adsorption analysis but, in

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•It is necessary to emphasize that Figure 2 is not connected with the curves shown on Figures 3-5. Actually, Figure 2 relates to a system of normal-paraffins + isoparaffins, while on Figures 3-5 a comparison is made of the isotherms of two systems: normal paraffins and commercial paraffins.

••It is of interest to quote the following example illustrating the efficiency of graphical extrapolation. Kolthoff and Kahn [22] have studied the adsorption of benzene solutions of butadienestyrene rubber on graphone. For one rubber the adsorption isotherm terminated in a horizontal section, while for the other it terminated in a sloping section; this behavior was attributed to the fact that in these rubbers, in addition to the sol fractions there is present a micro-gel fraction which is poorly adsorbed by the charcoal. In actual fact, it was found that the amount of rubber remaining in solution, according to the last point on the sloping section, was approximately equal to (but always slightly less than) the amount of the micro-gel fraction found by direct analytical methods. We extrapolated the sloping sections of the isotherms obtained by Kolthoff and Kahn to zero graphone content, and became convinced thereby that the amount of micro-gel in rubber calculated in this way, is almost in complete agreement with the analytically determined amounts.

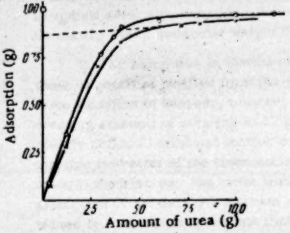

Fig. 5. Adsorption of paraffin No. 2 from CCl_4: x) original paraffin; O) purified paraffin; □) initial amount of paraffin in solution.

most cases, are somewhat lower. Even lower results were obtained when the Rosenberg, Genekh, Nikitina method was used. Presumably, for low contents of the iso-compounds, both sources of error suggested in [10, 14] as being characteristic of the analytical technique involving urea, namely dissociation of the complex and capture of the iso-compounds, compensate one another to a considerable extent. It is of interest to establish how complete such compensation would be in the case of analysis of compounds containing large amounts of iso-compounds, such as ceresines. We think that it is essential to emphasize that the techniques involving urea which have been suggested hitherto are equivalent to the study of one point on the adsorption isotherm of normal hydrocarbons by urea. Meanwhile, from the experimental results adduced in the present article, it follows that one well-defined conclusion regarding the content of normal hydrocarbons in paraffins can be made on the basis of the study of all the adsorption isotherms.

The method described is simple to carry out and permits work with small amounts of materials. We have obtained satisfactory results during work with 15 ml of solutions containing 0.25 g of paraffins. Since the method only demands analysis of equilibrium solutions, it is free from such operations as washing the complexes, their transfer from one piece of apparatus to another, decomposition of the complexes, and quantitative extraction of the paraffin. All these operations, particularly when working with small quantities, unavoidably lead to appreciable errors. It should also be borne in mind that during decomposition of the hydrocarbon complex, stable colloidal dispersions are often formed, this being a reason for the partial loss of paraffin.

TABLE

Expt. No.	Designation of test paraffin	% Normal hydrocarbons (by adsorption analysis)	% Normal hydrocarbons, Hessler and Meinhardt method [10]	% Normal hydrocarbons by other methods
1	GOST (TU) 215-51, series 51-8, homogenized, m.p. 51°	86.5 (Solvent C_6H_6) 86.5 (Solvent CCl_4)	89.5	83 (Rosenberg's method [14]) 90 ($H_2SO_4 + P_2O_5$ [3])
2	GOST (TU) ORU 40-55 Paraffin, purified preparation for laboratory work	87.0 (Solvent C_6H_6) 87.0 (Solvent $C_6H_5CH_3$) 88.0 (Solvent CCl_4)	86.0	83 ($H_2SO_4 + P_2O_5$ [3])
3	GOST (TU) 215-51, series 52-5, homogenized, m.p. 50°	82.5 (Solvent C_6H_6)	81.0	–
4	GOST (TU) 215-51, series 52-113, homogenized, m.p. 51°	91.0 (Solvent C_6H_6)	90.0	–

In conclusion we should like to make the point that on the basis of the considerations advanced in this article, it should be possible to determine iso-hydrocarbons with weakly branched chains in paraffins. We hope to discuss this question separately.

SUMMARY

1. A study has been made of the adsorption on urea of benzene solutions of narrow fractions of normal hy-

drocarbons isolated from commercial paraffins. The experimental results obtained can be described by the Langmuir adsorption equation. Adsorption coefficients and the limiting value of the adsorption increase with increasing mean molecular weight of the fractions.

2. The adsorption isotherms of a number of commercial paraffins on urea have been studied, as well as those of paraffins purified from iso-paraffins; the adsorption experiments were carried out from solutions of these paraffins in benzene, toluene, and carbon tetrachloride for constant concentrations of the paraffin, and increasing amounts of urea (up to 12 g/g of paraffin). The isotherms of the purified paraffins terminate in a clearly defined horizontal section corresponding to complete adsorption of the dissolved paraffin, while the adsorption isotherms of the commercial samples, for equal additions of urea, terminate in linear sections inclined toward the abscissa; the latter testifies to the fact that the adsorption process is composed of two processes: adsorption of normal-hydrocarbons and adsorption of iso-hydrocarbons. It has been shown that the ordinate obtained by extrapolating the last inclined section of the isotherm to zero urea content is a measure of the content of normal-hydrocarbons in the test paraffin. The analytical results obtained in this way are independent of the nature of the solvent; this fact testifies to the reliability of the method.

3. The methods described in the literature for the determination of normal-hydrocarbons by means of urea give, as a rule, somewhat low results. These methods are equivalent, in essence, to the study of only one point on the isotherm, while a well-defined conclusion regarding the content of normal hydrocarbons in commercial samples can only be made, as is evident from the results of the work described here, on the basis of the study of all the adsorption isotherms.

4. The method suggested is simple from the experimental point of view; it can be carried out with small amounts of materials, and is based on the analysis of equilibrium solutions. Consequently, it is free from errors connected with the transfer, washing, and decomposition of the complex formed by the interaction of urea and the hydrocarbons.

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ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF NAPHTHALENE AND α- AND β-CHLORONAPHTHALENES

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The starting material for the synthesis of α-naphthyltrialkylsilanes is technical α-chloronaphthalene which, in addition to small amounts of naphthalene, contains about 10% β-chloronaphthalene. As a result of this, the synthesized product contains β-naphthyltrialkylsilane as an impurity in the α-naphthyltrialkylsilane. Direct synthesis is carried out at a high temperature and in the presence of catalysts which favor the isomerization of the α- and β-derivatives. Thus, in the final product obtained, the contents of the α- and β-isomers will depend on the conditions used for the synthesis. Accordingly, a method for the quantitative determination of mixtures of naphthalene, α- and β-chloronaphthalenes, α- and β-naphthyltrichlorosilanes, and α- and β-naphthyltrialkylsilanes is of practical interest.

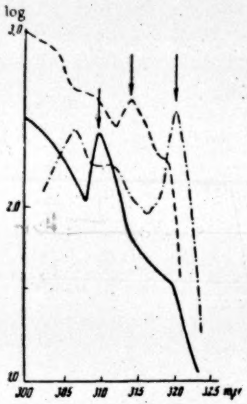
The present article contains a description of a method we have developed for the quantitative determination of naphthalene, α- and β-chloronaphthalenes in each others presence. Since the chemical properties of the α- and β-isomers are very close to each other, a chemical analysis of mixtures of these isomers is very difficult. Zil'berman [1] and Wibaut [2, 3] have suggested determination of the α- and β-isomer contents in each others presence by melting point diagrams of binary mixtures of α- and β-chloronaphthalenes; this method, however, is very cumbersome and is not accurate enough. Moreover, the presence of free naphthalene in these mixtures complicates determination. Accordingly, for the analysis of mixtures of naphthalene, and α- and β-chloronaphthalenes, we used an ultraviolet spectrophotometric method. Characteristic absorption bands are observed in the ultraviolet absorption spectra of isomeric naphthalene derivatives (Table 1) [4, 5].

TABLE 1

Compound	Absorption maximum, in mμ	Compound	Absorption maximum, in mμ
α-Chloronaphthalene	314	β-Chloronaphthalene	320
α-Methylnaphthalene	314	β-Methylnaphthalene	319
α-Naphthonitrile	315	β-Naphthonitrile	324
α-Naphthol	314	β-Naphthol	325

It can be concluded from the results given in Table 1 that an absorption band is observed in the spectra of the α-isomers at 314 mμ, while in the case of the β-isomers, this band is displaced somewhat and is located at 320 mμ. This should permit identification of each isomer in a mixture. An absorption band is found at 310 mμ in the case of naphthalene itself; this should, accordingly, serve as a means of identifying naphthalene. The ultraviolet absorption spectra of naphthalene, and of α- and β-chloronaphthalenes are shown in the diagram.

The ultraviolet absorption spectra of the test materials were taken by means of a SF-4 quartz photoelectric spectrophotometer; the test materials were dissolved in absolute ethanol. The starting materials used for developing the quantitative method were: chemically pure naphthalene (m.p. 80.1°), chemically pure β-chloro-



Determination of naphthalene, and α- and β-chloronaphthalenes by an ultraviolet spectrophotometric method: ——) naphthalene; ----) α-chloronaphthalene; —·—·—) β-chloronaphthalene.

naphthalene (m.p. 56°), and α-chloronaphthalene freed from β-chloronaphthalene as an impurity by a three-fold freezing out of technical α-chloronaphthalene.* The β-chloronaphthalene content of the α-chloronaphthalene was determined by means of melting point diagrams of binary mixtures of the α- and β-isomers. The results for the melting point diagrams for mixtures of α- and β-isomers were taken from the work of Wibaut and Bloem [2, 3, 6]. The content of residual β-chloronaphthalene in the α-chloronaphthalene did not exceed 2.7%. The boiling point of the purified α-chloronaphthalene was 121° at 12 mm residual pressure, while the setting temperature was −3.3°. Each test solution was tested for its conformity to the Beer law, for a concentration range from $1 \cdot 10^{-3}$ mole/liter to $5 \cdot 10^{-3}$ mole/liter in the wavelength region 310-320 mμ.

Since the test components of the mixture were found to conform to Beer's law, for the calculation of the content of each component, use was made of a formula relating optical density D of the mixture and the optical densities D_1, D_2 and D_3 of the components of the mixture in a definite spectral region,

$$D = D_1 + D_2 + D_3. \tag{1}$$

Since D = Kcd, where K is the absorption coefficient of a mixture of the component, c is the concentration, and d is the thickness of the layer, then Formula (1) can be written in the form:

$$D = (K_1c_1 + K_2c_2 + K_3c_3)\,d. \tag{2}$$

Having experimentally determined the values of the optical density of mixtures of the three components at wavelengths λ_1, λ_2 and λ_3, three equations can be compiled:

$$\begin{aligned} D_{\lambda_1} &= (K_{1\lambda_1}c_1 + K_{2\lambda_1}c_2 + K_{3\lambda_1}c_3)\,d; \\ D_{\lambda_2} &= (K_{1\lambda_2}c_1 + K_{2\lambda_2}c_2 + K_{3\lambda_2}c_3)\,d; \\ D_{\lambda_3} &= (K_{1\lambda_3}c_1 + K_{2\lambda_3}c_2 + K_{3\lambda_3}c_3)\,d, \end{aligned}$$

where $K_1\lambda_1$, $K_1\lambda_2$, $K_1\lambda_3$ are the absorption coefficients of the first component at λ_1, λ_2 and λ_3; $K_2\lambda_1$, $K_2\lambda_2$, $K_2\lambda_3$ are the absorption coefficients of the second component at λ_1, λ_2 and λ_3 and $K_3\lambda_1$, $K_3\lambda_2$ and $K_3\lambda_3$ are the absorption coefficients of the third component at λ_1, λ_2, and λ_3; c_1, c_2 and c_3 are the concentrations of the components of the mixtures; d is the thickness of the layer. Having experimentally determined the values of the optical density of mixtures at λ_1, λ_2 and λ_3, it is possible to calculate the concentrations c_1, c_2 and c_3, by solving the system of three equations with three unknowns. The values of the absorption coefficients of the components of a mixture at λ_1, λ_2 and λ_3 should be determined beforehand [7].

For the analysis of mixtures of naphthalene, and α- and β-chloronaphthalenes, the optical density of mixtures was measured at λ = 320 mμ (the absorption maximum for naphthalene), at λ = 314 mμ (the absorption maximum for α-chloronaphthalene) and at λ = 320 mμ (absorption maximum for β-chloronaphthalene). The values of the absorption coefficients of naphthalene, and of α- and β-chloronaphthalenes, at wavelengths of 310, 314 and 320 mμ (the so-called key absorption coefficients) were determined by measuring the optical density of solutions of the materials to be determined, at known concentrations of the latter, in the ultraviolet. Five solutions with varying concentrations of each test material were prepared and the mean values of the absorption coefficients taken; the latter were calculated by means of the formula $K = D/cd$, where D is the optical density of the solution, c is the concentration in grams/liter, and d is the thickness of the layer in cm^3. The results obtained are summarized in Table 2.

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* The preparations of naphthalene, α- and β-chloronaphthalenes were kindly given to us by N.M. Przhiialgovskaia, a co-worker in the D.I. Mendeleev Moscow Chemicotechnological Institute (Department of Intermediate Products and Dyes).

TABLE 2

Compound	K_{310}	K_{314}	K_{320}
Naphthalene	1.842	0.543	0.136
α-Chloronaphthalene	2.061	2.083	0.889
β-Chloronaphthalene	1.451	1.021	1.940

On the basis of the mean values of the calculated key coefficients, three equations of the general type given below were obtained:

$$\frac{D_{310}}{d} = 1.842\,c_1 + 2.061\,c_2 + 1.451\,c_3,$$

$$\frac{D_{314}}{d} = 0.543\,c_1 + 2.083\,c_2 + 1.021\,c_3,$$

$$\frac{D_{320}}{d} = 0.136\,c_1 + 0.889\,c_2 + 940\,c_3,$$

where c_1, c_2 and c_3 are the concentrations of naphthalene, and α- and β-chloronaphthalenes respectively in the solution, in grams/liter; D_{310}, D_{314} and D_{320} are the values of the respective optical densities of the test solutions at 310, 314 and 320 mμ; d is the thickness of the layer in cm^3.

By means of these three equations, a determination of the concentations of naphthalene, and α- and β-chloronaphthalenes when all three were present together was carried out; the mixtures were dissolved in absolute ethanol. For this purpose, three mixtures were prepared in which the concentrations of the various components were varied, and these concentrations determined by the ultraviolet spectrophotometric method.

TABLE 3

Composition of the mixture	Known concentration, in %	Calculated concentration, in %	D_{310}	D_{314}	D_{320}	Error, in %
Naphthalene	1.72	1.70	0.805	0.520	0.430	−1.16
α-Chloronaphthalene	1.30	1.32				+1.53
β-Chloronaphthalene	1.52	1.51				−0.65
Naphthalene	1.86	1.84	0.860	0.550	0.480	−1.07
α-Chloronaphthalene	1.30	1.24				−4.61
β-Chloronaphthalene	1.76	1.80				+2.27
Naphthalene	1.72	1.73	0.812	0.485	0.412	+0.58
α-Chloronaphthalene	1.15	1.15				0
β-Chloronaphthalene	1.76	1.74				−1.13

Table 3 contains the known and calculated values for the concentrations of the components in the mixtures, as well as the values of the optical density which were determined spectrophotometrically.

The results obtained show that the small amount of α-chloronaphthalene present as an impurity in the β-chloronaphthalene which was used for establishing the "key" coefficients, has only very little effect on the accuracy of the results obtained.

SUMMARY

A method has been developed for the quantitative determination of naphthalene, and α- and β-chloro-

naphthalenes; it is based on an ultraviolet spectrophotometric method in which the optical density of solutions of these compounds in absolute ethanol is measured at 310, 314 and 320 mμ.

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SPECTROPHOTOMETRIC DETERMINATION OF CROTONALDEHYDE IN THE ULTRAVIOLET

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At the moment there is no satisfactory method for the quantitative determination of crotonaldehyde in the presence of other organic compounds such as acetaldehyde, acetone, acetylene, and acetic acid; it is precisely in such mixtures that crotonaldehyde occurs in the products of certain organic synthesis reactions, e.g., in the synthetic rubber industry. Existing methods [1, 2] which are based on the reactions of functional groups are not selective for crotonaldehyde, so that it is impossible to determine this aldehyde in the presence of unsaturated as well as carboxyl compounds. Naturally, the development of selective methods for the quantitative determination of crotonaldehyde is a real problem.

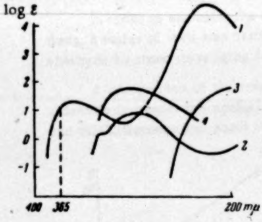

Fig. 1. Absorption spectra of solutions of crotonaldehyde (1), acetaldehyde (2), acetic acid (3), and acetone (4) in water.

The work described in the present article is one of the attempts made to solve this problem, the assumption made being that one approach should be photometric determination in the ultraviolet.

Solutions of crotonaldehyde in aqueous and nonaqueous media to which various amounts of acetaldehyde, acetic acid, acetone, and acetylene had been added were studied.

A comparison of absorption curves in the ultraviolet by crotonaldehyde, acetaldehyde, acetic acid, acetone, and acetylene (Fig. 1), taken from the literature [3], shows that at 365 mμ only crotonaldehyde absorbs. This means that it should be possible to determine crotonaldehyde photometrically without preliminary separation from the organic compounds listed above.

The work was carried out on a visual instrument suggested previously [4]. Quartz cells with a layer thickness of 25 mm were used.

The experimental technique consists of preparing various solutions with known contents of crotonaldehyde and measuring the optical density of the solutions. Each solution was diluted to half its original concentration (by addition of water or the appropriate solvent), and optical density measurements repeated. Such dilutions were repeated several times. The maximum crotonaldehyde concentration in aqueous solutions was 12.8% by volume, which is approximately equal to a saturated solution of crotonaldehyde in water.

Crotonaldehyde was prepared by dehydration of the aldol of orthophosphoric acid [5]; its boiling point was 101°, while n_D^{20} was 1.4364. According to published results the boiling point is 101.3-102.0° and n_D^{20} 1.4356 [6]. The crotonaldehyde content of the product obtained, as determined by the hydroxylamine-hydrochloride method [2] was 98.1%, while by the bromide-bromate method [7], its content was 99.1%.

Acetaldehyde was prepared by depolymerization of paraldehyde in the presence of concentrated sulfuric acid (b.p. 21°).

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*N.M. Slastenova participated in the experimental work.

Acetone (analytical grade) and acetic acid (glacial) were the commercial products; the acetylene was taken from a cylinder.

Determination of Crotonaldehyde in Aqueous Solutions

First of all the concentration range over which aqueous solutions of crotonaldehyde conformed to Beer's law was established. The experimental results which are shown in Figure 2 indicate that this range is 0.1-12.8% by volume, accordingly, crotonaldehyde can be determined photometrically over this range.

TABLE 1

Effect of Acetaldehyde on the Optical Density of Aqueous Solutions of Crotonaldehyde

Crotonaldehyde, % by volume	Acetaldehyde, % by volume	Optical density
12.8	5.0;10.0;15.0;20.0;25.0	2.25;2.30;2.45;2.50;2.50
6.4	2.5; 5.0; 7.5;10.0;12.5	1.12;1.26;1.26;1.26;1.30
3.2	1.75;2.5;3.7;5.0;6.2	0.59;0.62;0.64;0.64;0.64
1.6	0.87;1.75;1.8;2.5;3.1	0.32;0.34;0.32;0.38;0.38
0.8	0.43;0.87;0.9;1.25;1.5	0.18;0.19;0.19;0.20;0.20
0.4	0.22;0.43;0.45;0.62;0.7	0.12;0.14;0.14;0.14;0.13
0.2	0.11;0.22;0.22;0.31;0.35	0.07;0.07;0.08;0.08;0.07
0.1	0.05;0.11;0.11;0.15;0.17	0.03;0.04;0.04;0.04;0.04

In order to establish the effect of acetaldehyde on the determination of crotonaldehyde in aqueous solutions, a series of tests was carried out with solutions of crotonaldehyde of different concentrations, to which acetaldehyde in amounts ranging from 5 to 25% by volume had been added.

A comparison of the results given in Table 1 with those shown on Figure 2 shows that the presence of acetaldehyde increases the optical density of crotonaldehyde solutions as compared with pure solutions of the latter, and this difference increases with increasing concentrations of acetaldehyde and crotonaldehyde.

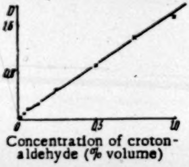

Fig. 2. Relation between optical density and crotonaldehyde concentration.

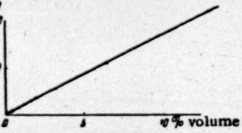

Fig. 3. Relation between optical density and crotonaldehyde concentration in acetaldehyde and acetone: x) solution of crotonaldehyde in acetone; o) solution of crotonaldehyde in acetaldehyde.

Next, a series of tests was carried out with solutions with low concentrations of crotonaldehyde, in order to establish the limits of applicability of the method for the determination of crotonaldehyde in the presence of acetaldehyde. These experiments showed that determination is possible for crotonaldehyde contents up to 0.4% by volume when the acetaldehyde concentration is not greater than 20% by volume; for a crotonaldehyde concentration of up to 1.6% by volume, the limiting concentration of acetaldehyde must be decreased to 15% by volume; while for a crotonaldehyde concentration of up to 3.2% by volume, the limiting acetaldehyde concentration should not be greater than 10% by volume.

In the case of low concentrations of acetaldehyde (below 5% by volume) and large concentrations of crotonaldehyde (above 3% by volume), as our experiments showed, the limiting concentration of acetaldehyde should not exceed 3.5% by volume; or more accurately, at crotonaldehyde concentrations up to 4% by volume, the maximum concentration of acetaldehyde which will not interfere with the determination is 5% by volume; while for crotonaldehyde concentrations up to 12.8% by volume, the limiting acetaldehyde concentration is 3.5% by volume.

Acetic acid starts to affect determination of crotonaldehyde when the concentration of the former exceeds 4.0% by volume for a crotonaldehyde concentration of 12.8% by volume, and affects determination when its concentration is 10% by volume when the crotonaldehyde concentration is 3.2% by volume.

Acetone increases the results of determination slightly when solutions contain more than 2.0% by volume for a crotonaldehyde concentration of 12.8% by volume.

When all these compounds are present simultaneously, in the case where the concentration of the crotonaldehyde is at its maximum (12.8% by volume), the maximum permissible amounts of the impurities amount to 2.0% by volume acetaldehyde, 2.0% by volume acetic acid, and 1.0% by volume acetone.

Measurements of the optical density of aqueous solutions of crotonaldehyde and acetaldehyde, containing 6.0-0.4 and 3.0-16.0% by volume of these components, respectively, saturated with acetylene at atmospheric pressure and room temperature, showed that acetylene does not interfere with crotonaldehyde determination.

In order to check on the method, analyses were carried out on synthetic mixtures containing crotonaldehyde together with acetaldehyde, acetic acid, and acetone in aqueous solution (Table 2).

Determination of Crotonaldehyde in Nonaqueous Solutions

The optical density of solutions of crotonaldehyde in acetaldehyde and acetone almost coincides and is linearly dependent on the concentration over a wide range; this means that crotonaldehyde can be determined in these nonaqueous solvents (Figure 3).

TABLE 2

Determination of Crotonaldehyde in Synthetic Mixtures

Content in aqueous solution, in % by volume				Crotonaldehyde found, in % by volume
crotonaldehyde	acetic acid	acetone	acetaldehyde	
0.3	–	–	4.0	0.3
0.4	0.2	–	8.0	0.4
0.8	0.4	–	8.0	0.8
1.2	0.5	–	16.0	1.2
1.2	–	0.2	18.0	1.2
2.4	–	0.4	14.0	2.5
3.6	0.2	–	20.0	3.7
10.0	0.4	–	24.0	10.0

TABLE 3

Determination of Crotonaldehyde in Acetaldehyde

Crotonaldehyde taken, in % by volume	Crotonaldehyde found, in % by volume	Absolute error, in %
0.20	0.26	+0.06
0.40	0.40	–
0.50	0.54	+0.04
0.80	0.82	+0.02
1.00	1.02	+0.02

The results for determination of crotonaldehyde in acetaldehyde shown in Table 3 exhibit good agreement.

The presence of acetic acid in acetaldehyde or acetone strongly depresses the results for determination of crotonaldehyde; accordingly, these solvents should be free from acetic acid when they are to be used for crotonaldehyde determination. Acetylene does not interfere when these nonaqueous solvents are used, as in the case of aqueous solutions.

Irradiation for up to eight hours with ultraviolet does not affect the density of the working solutions.

SUMMARY

1. A method has been developed for the spectrophotometric determination in the ultraviolet of crotonaldehyde in the presence of acetaldehyde, acetic acid, acetone, and acetylene, in aqueous solutions.

2. Conditions for the photometric determination of solutions of crotonaldehyde in acetaldehyde, acetone, and acetic acid have been investigated.

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*Original Russian pagination. See C.B. translation.

BRIEF COMMUNICATIONS

POLAROGRAPHIC DETERMINATION OF ETHYL MERCURIC CHLORIDE IN GRANOSAN

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The possibility of reducing certain organometallic compounds on a dropping mercury electrode has been demonstrated by a number of authors [1-3]. In the work described here reduction of ethyl mercuric chloride (C_2H_5HgCl) on a dropping mercury electrode was studied, with the aim of determining this compound quantitatively in granosan (preparation NIUIF-2).

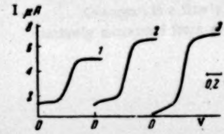

Fig. 1. Polarograms for the reduction of ethyl mercuric chloride in a supporting electrolyte of 0.2 N hydrochloric acid (Curves 1 and 2), and a polarogram obtained after treatment of granosan (Curve 3).

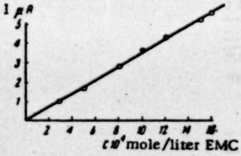

Fig. 2. Calibration line for determination of ethyl mercuric chloride in a supporting electrolyte of 0.2 N hydrochloric acid.

The work was carried out on a visual type polarograph of the Gorky Scientific Research Institute of Chemistry [4]; the mirror galvanometer used had a sensitivity of $0.6 \cdot 10^{-9}$ amp/mm/m scale reading. The characteristics of the capillary used were $m^{2/3} t^{1/6} = 2.48\ mg^{2/3} \cdot sec^{-1/2}$.

The ethyl mercuric chloride (EMC) used, which was twice recrystallized, had a melting point of 192°, in good agreement with the published results. A 0.005 M alcoholic solution of this compound was prepared from this product.

During a study of the reduction of ethyl mercuric chloride on a dropping mercury electrode in supporting electrolytes of HNO_3, HCl, KCl, KNO_3, and LiCl it was found that the best supporting electrolyte was 0.2 N hydrochloric acid. In this supporting electrolyte ethyl mercuric chloride gives clear-cut, well-defined waves at a half-wave potential of −0.4 volt relative to the saturated calomel electrode.

A calibration curve was used for obtaining quantitative characteristics. Solutions of ethyl mercuric chloride with concentrations ranging from $3 \cdot 10^{-4}$ to $1.5 \cdot 10^{-3}$ m/liter were prepared. The alcohol concentration was 30% in all the solutions. Solutions prepared in this way, after hydrogen had been bubbled through them, were then polarographed at a galvanometer sensitivity of $S = 1/50$.

In Figure 1 (Curves 1 and 2) are shown polarograms for ethyl mercuric chloride, while in Figure 2 is shown the calibration curve for its determination in a supporting electrolyte of 0.2 N hydrochloric acid.

Technical preparations of ethyl mercuric chloride may contain small amounts of mercuric chloride. During reduction of ethyl mercuric chloride and mercuric chloride in each others presence, two separate, well-defined curves are obtained, one of which corresponds to the reduction of mercuric chloride and starts at zero applied emf, while the other corresponds to the reduction of ethyl mercuric chloride (Figure 3, Curve 1). The mercuric chloride concentration was changed from $1.6 \cdot 10^{-5}$ to $1.6 \cdot 10^{-4}$

m/liter, while the concentration of ethyl mercuric chloride was kept constant at 0.002 m/liter.

For a mercuric chloride content which was one-tenth to one-hundredth of the ethyl mercuric chloride, the diffusion current of the latter was found to be independent of the mercuric chloride concentration. When, however, both components were present in approximately equal amounts – and particularly when there was more mercuric chloride present than ethyl mercuric chloride – the diffusion current of ethyl mercuric chloride increased considerably with increasing mercuric chloride concentration.

Ethyl mercuric chloride does not affect the diffusion current of mercuric chloride. When polarograms were taken of solutions with a constant concentration of mercuric chloride of $0.8 \cdot 10^{-3}$ m/liter, and with varying concentrations of ethyl mercuric chloride, the diffusion current of mercuric chloride remained constant, while that for ethyl mercuric chloride was directly proportional to the concentration of the latter.

Since the amounts of mercuric chloride which are present in granosan are small, simultaneous determination of ethyl mercuric chloride and mercuric chloride is completely possible.

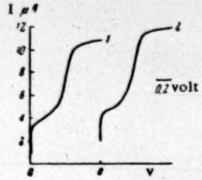

Fig. 3. Polarogram for ethyl mercuric chloride and mercuric chloride in a supporting electrolyte of 0.2 N hydrochloric acid (Curve 1), and the polarogram for a solution obtained after treatment of granosan to which mercuric chloride was added.

Granosan is a finely-ground mixture of technical talc and ethyl mercuric chloride. The latter is quantitatively extracted from granosan with ethanol by refluxing on a water bath (Table 1).

TABLE 1

Ethyl mercuric chloride added to the talc, in g	Ethyl mercuric chloride determined polarographically, in g	Error, in %
0.0132	0.0145	+9.8
0.0172	0.0165	−4.0
0.0388	0.0397	+2.3
0.0306	0.0311	+1.6

TABLE 2

Granosan sample 1799		Granosan sample 1800	
sample weight, in g	ethyl mercuric chloride found, in %	sample weight, in g	ethyl mercuric chloride found, in %
3.0074	1.64	3.0001	1.69
3.0029	1.71	3.0009	1.71
2.0006	1.61	2.0004	1.82

Mercuric chloride can be determined at the same time as ethyl mercuric chloride. Nevertheless, when polarograms were taken of solutions obtained by extraction of ethyl mercuric chloride from granosan, the wave for mercuric chloride was not observed (Figure 1, Curve 3).

Experimental procedure for determination of ethyl mercuric chloride. 3 g of granosan and 25-30 ml of ethanol were refluxed in a round-bottom flask on a water bath for ten minutes. After cooling, the residue was filtered off and washed a few times with hot alcohol and the filtrates collected in a standard flask; when the temperature was 20° the volume was made up to the mark with alcohol. 2 ml of this solution was placed in an electrolyzer and 3 ml of 0.3 N hydrochloric acid added; after the solution had been purged with hydrogen for 30 minutes, polarograms were taken at S = 1/50. The concentration of ethyl mercuric chloride was then determined by means of the calibration curve. Satisfactory results were obtained during determination of ethyl mercuric chloride in production samples of granosan (Table 2). A gravimetric method, GOST-5150-49, gave higher results because technical talc usually gives a solid residue (an increase in weight) of up to 0.35%, presumably elemental sulfur.

SUMMARY

Reduction of ethyl mercuric chloride on a dropping mercury electrode has been studied and conditions have been established for its quantitative determination in granosan. Conditions have been found for the simultaneous, quantitative determination of ethyl mercuric chloride and mercuric chloride.

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A QUALITATIVE REACTION FOR META-AMINOPHENOL AND PARA-AMINOSALICYLIC ACID

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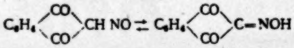
We have observed that on heating a solution of meta-aminophenol in glacial acetic acid with 2-nitrosoindanedione-1,3, a green fluorescence appears. When the concentration of the meta-aminophenol in solution is high enough, a red color appears. When the meta-aminophenol concentration is very low, the fluorescence only appears on cooling the solution. A small excess of nitrosoindanedione (up to three moles per mole of meta-aminophenol) favors the reaction; a large excess of this reagent, however, decreases the sensitivity of the reaction.



$$C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}CH\ NO \rightleftharpoons C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}C{=}NOH$$

The limiting dilution of meta-aminophenol at which the fluorescence is still observable is 1:40,000. In solution in ethanol, ether, benzene, dioxan , dilute acetic acid, and also in glacial acetic acid containing a small amount of acetic anhydride, the fluorescence does not appear.

Ortho-aminophenol and para-aminophenol do not give this reaction, and do not interfere when they are present in amounts which are one-hundred times that of the meta compound. When large amounts of the ortho- and para-compounds are present, the solution becomes intense-red and the fluorescence does not appear. The following compounds do not give a green fluorescence with nitrosoindanedione: phenol, resorcinol, aniline, and many other aromatic and aliphatic primary, secondary and tertiary amines; this reaction therefore appears to be specific for meta-aminophenol.

Para-aminosalicylic acid (PASA) on heating is readily decarboxylated to give meta-aminophenol. Accordingly, one might expect that PASA would also give a positive reaction with nitrosoindanedione. In fact, when PASA is heated in glacial acetic acid with nitrosoindanedione, carbon dioxide is liberated and the liquid gradually acquires a green fluorescence. Since decomposition of PASA does not occur immediately, in the case of low concentrations of PASA, it is necessary therefore to prolong the heating. The limiting dilution of PASA at which fluorescence can be detected is 1: 28,000. The ratio of the limiting sensitivities of meta-aminophenol and PASA (40,000: 28,000) corresponds approximately to the inverse ratio of their molecular weights (153: 109), from which it follows that PASA almost quantitatively decomposes to give meta-aminophenol under the reaction conditions used.

Preparation of Nitrosoindanedione

1. Rapid preparation of small amounts [1]. Indanedione-1,3 is dissolved in aqueous alkali, a solution of sodium nitrite is added and the mixture slowly poured into dilute sulfuric acid. The precipitate which settles out is crystallized from glacial acetic acid.

2. Preparative method [2]. To 8 g of indanedione in 300 ml of dilute alkali contained in a flask provided with a mechanical stirrer is added 4 g of sodium nitrite. The flask is cooled with ice, and hydrochloric acid added dropwise with constant stirring until the reaction mixture gives an acid reaction. The mixture is then agi-

tated at room temperature for a further 45 minutes. The precipitate which separates out is recrystallized from glacial acetic acid. The yield is 8.4 g of nitrosoindanedione (87% of theory); the compound is in the form of yellow crystals with a melting point of about 200°; the melting point depends partly on the rate of heating [3], and also on the solvent used for its recrystallization [4]. Small amounts can be recrystallized from water as well.

The color reaction itself. 2-3 mg of meta-aminophenol is dissolved in 5 ml of glacial acetic acid, and a few milligrams of nitrosoindanedione is then added and the mixture boiled for one minute; the mixture is finally cooled under the tap. A green fluorescence should appear. For smaller amounts of meta-aminophenol, heating should be continued for a longer time. During detection of PASA in the same way, heating should also be carried out for a longer time; for limiting concentrations of PASA, this period should be as much as ten minutes.

SUMMARY

Meta-aminophenol and para-aminosalicylic acid give a green fluorescence on heating in glacial acetic acid with nitrosoindanedione.

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COLOR REACTIONS OF PHENOLS WITH XANTHYDROL

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Xanthydrol is normally used as a reagent for establishing the identity of amines, urethanes, and barbituric acid derivatives [1]. With these classes of compounds xanthydrol forms xanthyl derivatives which can be readily purified, and have sharp melting points. Xanthydrol is also known to react with mono- and diphenols [2, 3], colorless, crystalline condensation products being formed. This latter reaction is of no analytical significance since it proceeds very slowly and gives a small yield of final products which are rather difficult to isolate and purify.

We were the first to observe that xanthydrol in alcoholic solution, in the presence of mineral acid, is capable of reacting with phenols to give colored products. The color reaction of xanthydrol with phenols is more specific than the well-known reaction with ferric chloride. Many phenol derivatives which give colored products with the latter reagent do not react with xanthydrol.

Xanthydrol was prepared by the reduction of pure xanthone by means of sodium amalgam [4]. The damp preparation was dried at 40-50° to constant weight and then dissolved in alcohol. The reagent was found to be still usable after six months storage.

The reaction between phenols and xanthydrol is best carried out as follows. 2-3 mg of test material is introduced into a test tube and 0.5 ml of a 5% solution of xanthydrol in alcohol added. The mixture is gently warmed to dissolve the phenol, and two drops of dilute or concentrated hydrochloric acid added; the contents of the test tube are then boiled for several seconds. Intense colors should then develop.

On heating the xanthydrol solution with two drops of hydrochloric acid a yellow color appears which disappears on cooling the reaction mixture. The color obtained on heating a phenol with xanthydrol and hydrochloric acid, however, is very stable and there is no decolorization even after several days.

Colors of the Reaction Products Formed from Phenols and Xanthydrol in the Presence of Hydrochloric Acid

Test compound	Color	Sensitivity, in γ/ml	Test compound	Color	Sensitivity, in γ/ml
Phenol	Raspberry-red	25	Guaiacol	Violet-red	50
α-Naphthol	Dark green	5	Resorcinol	Blue-violet	10
β-Naphthol	Grass-green	10	Hexylresorcinol	Dark blue	–
o-Cresol	Bright red	4	Hydroquinone	Yellow-green	25
m-Cresol	Orange-red	5	Pyrogallol	Violet-red	2.5
Thymol	Wine-red	10	Phloroglucinol	Violet-blue	10
Carvacrol	Red	8	Tannin	Violet-red	–
Eugenol	Brown-red	–	Methyl salicylate	Rose	–
Pyrocatechol	Lilac	10			

The table contains the results obtained for the phenols which we studied. The reaction sensitivity increases sharply with decreasing pH of the reaction mixture. The reaction sensitivity was established as follows. 0.4 ml of an alcoholic solution of a phenol of an appropriate concentration was introduced into a test tube; this was followed by 0.4 ml of xanthydrol solution and 0.2 ml of hydrochloric acid (sp.gr. 1.18). The mixture was boiled for several seconds. After cooling, the color of the reaction mixture was noted.

It is evident from the table that not only unsubstituted phenols react with xanthydrol, but also their derivatives containing: a) alkyl groups (cresols, thymol, carvacrol, eugenol, hexylresorcinol); b) methoxy groups (guaiacol); and c) an ester group (methyl salicylate).

Color reactions with xanthydrol are not given by phenol derivatives containing: a) acid groups (salicylic acid, gallic acid, β-naphthol-3,6-disulfonic acid, 3-acetamino-4-hydroxyphenylarsonic acid); b) basic groups (p-aminophenol, adrenaline); c) halogens (tribromophenol); and d) nitro-groups (o- and p-nitrophenol, 2,4-dinitrophenol, and picric acid).

SUMMARY

Xanthydrol in alcohol solution, on being heated with phenols in the presence of hydrochloric acid gives colored products. This reaction can be used for identifying phenols. Reactions between xanthydrol and 17 phenols are described and the reaction sensitivity of most of them determined. Unsubstituted phenols and phenol derivatives containing alkyl or methoxy groups give a positive reaction with xanthydrol. Phenol derivatives containing halogens, carboxy, amino, and nitro groups do not give this reaction.

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THE USE OF A DC CURRENT FOR CERTAIN CHROMATOGRAPHIC STUDIES

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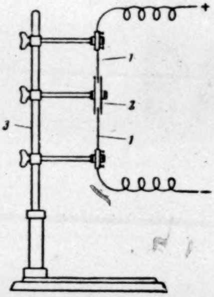
In the presence of a conducting medium in a column containing a sorbent with an appropriate reagent, it is possible to increase the sensitivity of the chromatographic method of detecting certain ions by passing a dc current through the column.

Into one end of the column packed with sorbent is passed a known amount of test solution and developer-reagent. When the solution does not moisten the contents of the column, the other end of the latter is placed in a small beaker, on the bottom of which is placed a filter paper soaked with distilled water. The water rises in the tube and, in the course of 10-15 minutes, moistens the sorbent. The tube is then fixed in a stand and two platinum needles are fitted into the column packing from both ends (diagram). Since the electrical conductivity of the column is very small, it is necessary to push the needles to a distance of not more than 1-1.5 cm into the sorbent. The platinum needles are connected to a dc supply with a fairly high voltage of 15 volts, sometimes even as high as 25 volts.



It is essential to remember that the experiments are being carried out with a weak current. The best results are obtained with a current of 0.01-0.02 amp. Increasing the current considerably led, in most cases, to uneven development of some parts of the column and, sometimes, even to the appearance of a noncharacteristic dark brown color.

Such a phenomenon was observed during detection of NO_2^- with α-naphthylamine.

When the technique described was used, positive results were obtained when the anode needle was placed into that end of the tube containing sorbent, through which the test solutions and developers were passed.

Using this technique experiments were carried out on the detection of several anions. In our studies the best results were obtained during the detection of NO_2^-.

Detection of NO_2^- by Formation of Azo Dyes

The amino compounds used were sulfanilic acid, p-nitroaniline and sulfanilamide, while the azo components used were α-naphthol, β-naphthol and α-naphthylamine. The sorbents used were chemically pure SiO_2 and Al_2O_3 which had been finely ground (sieve with 0.10 m/m mesh); it was found that SiO_2 was a better sorbent than Al_2O_3 from the point of view of sensitivity.

1) For the detection of NO_2^-, one part of α-naphthylamine, one part of sulfanilic acid, and ten parts of SiO_2 were mixed. 0.05 ml of the test solution was introduced by means of a micropipet into the packed column; this was followed by 0.05 ml of 5 N CH_3COOH. A red band was formed. The limit of identification of NO_2^- was found to be 0.01 γ NO_2^-. An electric current (voltage up to 25 volts) enhanced the intensity of the color but the

sensitivity remained almost the same.

2) For detection of NO_2^- with sulfanilamide and α-naphthylamine, using SiO_2 as sorbent (ratio 1:10), the limit of identification without using a current was found to be 0.04 γ NO_2^-, whereas when a current was used, the limit was found to be 0.02 γ NO_2^-. When a current was used the intensity of the color also increased, even at the limits of the first limit of identification of 0.04 γ. A red band was observed.

3) For detection of NO_2^- with sulfanilic acid and α-naphthol, and using Al_2O_3 as sorbent (in the proportion of 1:10), 0.05 ml of test solution was introduced into the column first; this was followed by 0.05 ml of 5 N CH_3COOH. A rose color was first formed, which subsequently changed to orange. The limit of identification without using a current was 0.12 γ NO_2^-, while on using a current (20 volts) the limit was 0.05 γ NO_2^-.

4) When detection of NO_2^- was carried out using sulfanilic acid and β-naphthol, and SiO_2 was used as the sorbent (in the proportion of 1:10) an orange band was formed. The limit of identification was 0.16 γ NO_2^-. Passage of an electric current had little effect on the reaction sensitivity.

5) For the detection of NO_2^- with p-nitroaniline and β-naphthol using SiO_2 as sorbent (in the proportion of 1:20), the limit of identification without a current was 0.2 γ NO_2^-, while with a current (15-20 volts) the limit was 0.08 γ NO_2^-.

6) Detection of NO_2^- with p-nitroaniline and β-naphthol, using SiO_2 as sorbent (in the proportion of 1:20), was less sensitive. The limit of identification without using a current was 1 γ NO_2^-, while with a current (15-20 volts) it was 0.16 γ NO_2^-. A red band was formed.

The enhanced sensitivity of the reactions indicated above when a dc current is used is, presumably, connected with the concentration of the reactants in the zone surrounding the anode.

SUMMARY

The sensitivity of the chromatographic method for detecting NO_2^- ions with sulfanilamide and sulfanilic acid can be increased by passing a dc current through a column packed with sorbent containing the appropriate reagent, as long as the column contains a medium which is conducting.

Received August 2, 1956

PETR ANDREEVICH VOLKOV

(October 1, 1889 – October 26, 1957)

Petr Andreevich Volkov was born on the 21st of October, 1889 in Cherepovets, Novgorod region; he finished at the chemical section of the Leningrad Polytechnical Institute in 1921.

From 1918 Volkov worked in the Academy of Sciences, starting in the Commission of Natural Resources (KEPS); he then transferred to the Radium College (KEPSe), which was changed to the State Radium Institute in 1922. In 1929 Volkov joined the Institute of Geological Sciences where he worked as a senior scientific worker till his death.

In 1936 he was awarded the degree of candidate of chemical sciences without defending his thesis. For carrying out government work he was awarded the order of the "Sign of Honor," and was awarded the order of Lenin for his long years of service.

Volkov was an outstanding analytical chemist and a talented technologist. Starting off with the solution of problems of an analytical and preparative character, Volkov applied them on a plant scale.

He was one of the pioneers of radium technology in Russia. His first scientific work was devoted to a study of equilibrium in solutions of barium and lead chlorides, and was carried out under the direction of V.G. Khlopin and N.S. Kurnakov. His important work on obtaining preparations containing a high percentage of radium formed a basis for a radium bank in the Radium Factory, in whose construction he took a leading part; he also organized a mine laboratory which he managed for two years (1924-1926).

He carried out a large amount of analytical work on ores and shales, and discovered and described a new mineral "tangeite."

From 1926 to 1934 Volkov occupied himself with problems relating to sulfur, and from 1933 to 1941 developed the technology of the Khibinsk ores; this included: methods of breaking down nepheline with sulfuric and sulfurous acids for the preparation of silica-gel and alum, a method for preparing the rare earths from lovchorite and apatite, and a method for extracting CaO from apatite, etc.

During the Second World War Volkov was head of the analytical laboratory of the Ural Branch of the Academy of Sciences in Sverdlovsk, while from 1944 onward he was at the Central Chemical Laboratory of the Institute of Geological Sciences.

Since 1946 Volkov has been engaged in special Government work, and carried on with this work until his death. Under his direction, methods were developed for the determination of small amounts of impurities in pure metallic uranium and, in conjunction with his students, he personally developed a neat and simple method of determining uranium which is characterized by high accuracy and the speed with which it can be carried out. This method is widely known in practice as "Volkov's Method."

There was nothing stereotyped about his work; the creative element was always present. He always shared his ideas, successes and failures with his comrades, and was never satisfied with what he had achieved, but always strove for perfection.

He turned his ideas to practical use by stubborn work, and by an infinite amount of experimental work, and succeeded in making things work which at first glance would seem to be impossible.

Although he was deeply interested in his work, outside the laboratory Volkov was a sociable, interesting person. He enjoyed the sincere respect and love of his companions at work and of numerous students.

I. Borneman

THE FOURTH CONFERENCE ON THE ANALYSIS OF THE NOBLE METALS

May 20-23, 1957

The Fourth Conference on the Analysis of the Noble Metals was held on May 20-23, 1957, in Sverdlovsk; it was convened by the N.S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences and by the Factory on the Treatment of Noble Metals, in conjunction with the Ministry of Finance of the USSR, the Ministry of Non-Ferrous Metals of the USSR, and by the Ural House of Technics. One hundred and eleven delegates participated. Thirty-two organizations were represented, while thirty-five reports and communications were read.

One section of the reports was devoted to questions on technical methods of analysis: "The Use of Thionalide and Thiourea for Determination of Rhodium and Iridium," by N.K. Pshenitsyn and I.V. Prokof'eva; "Recent Advances in the Chemical Analysis of Factory Materials," by Kh.I. Tsybulevskii and I.N. Firsova. This question was also dealt with in reports from representatives of various factories (M.S. Usova et al.). Several reports dealt with volumetric methods: "Volumetric Determination of Iron, Platinum and Iridium in Each Others Presence," by A.A. Grinberg; "A New Volumetric Method for the Determination of Silver in Alloys and Production Residues," by M.A. Chentsova, T.P. Iufa and V.G. Levian, etc.

A special session was devoted to spectrographic methods of analysis used at present in all refining factories. The reports of V.P. Khrapaia, V.L. Ginsburg, A.D. Gut'ko and N.N. Pankratov, A.D. Kuranov, N.P. Ruksh, M.M. Sviridova were devoted to the determination of all the noble metals, and of some impurities in concentrates, alloys, ores, and other materials. Some reports dealt with the preparation of poor samples for spectrographic analysis (S.M. Anisimov, K.A. Pomytov and E.I. Nikitina, N.L. Chentsova).

The applicability of assay methods (cupellation as a silver bead) for the determination of rhodium, iridium and ruthenium in ores and other products was discussed. In some instances, these elements are not concentrated completely in the silver bead. It turned out from the discussion that the method of copper assay as applied to materials containing iridium, rhodium or ruthenium has not been developed sufficiently (the report of S.K. Shabarin and I.D. Fridman).

Four reports dealt with polarographic methods and ion exchange: "A Polarographic Method of Determining Iridium," N.K. Pshenitsyn, N.A. Ezerskaia and V.D. Ratnikova; "Determination of Lead, Bismuth and Antimony in Refined Gold," E.K. Kuznetsova; "Methods of Determining Impurities in Platinoid Materials Based on Ion Exchange and Polarography," S.M. Anisimov, V.M. Klypenkov, P.G. Shulakov, V.N. Alianchikova and P.A. Gurin; and "Polarographic Determination of Some Platinum Metals on Solid Electrodes," Iu.S. Lialikov and M.B. Bardin.

A group of reports dealt with spectrophotometric and photocolorimetric methods of analysis: "Photocolorimetric Methods of Analyzing Platinum Metals (Refined)," V.K. Levian and T.P. Iufa; "A Study of Certain Spectrophotometric Methods of Determining Iridium and the Reactions Forming the Basis of these Methods," N.K. Pshenitsyn, S.I. Ginsburg and L.G. Sal'skaia; "A Photocolorimetric Method of Determining Rhodium in the Presence of Platinum," V.N. Aleksandrov; "Photocolorimetric Determination in the Presence of Silver," V.F. Barkovskii.

Two reports were given by V.B. Avilov – "Chromatographic Determination of Gold," and the "Effect of Complex Formation and the Acid-Alkali Equilibrium of the Medium on the Potentials of Systems."

The communication of V.V. Kosova and that of S.M. Anisimov, V.M. Klypenkov and V.P. Tsimbal dealt with the electrometric determination of silver in alloys and factory products.

M.S. Ruzhinkov demonstrated a technique for the determination of gold on a touchstone which has been used for several centuries, and gave details of a new method for testing palladium alloys on a touchstone.

Finally, the last group of reports dealt with physical methods of analysis: "Determination of the Chemical Composition of Ternary Alloys on the Basis of Physical Properties," A.A. Rudintskii; "Determination of the Chemical Composition of Binary Alloys on the Basis of EMF," A.P. Adakhovskii and V.M. Karbolin; "Quantitative Determination of Micro Amounts of Gold and Platinum Metals by a Radioactivation Method," A.I. Kulak and O.E. Zviagintsev; and "Apparatus and Methods for the Determination of Gases in Metals," Z.M. Turovtseva.

A report was finally given by D.G. Grebenkin a representative of the Ministry of Finance of the USSR on "The Role and Importance of Analysis in Production Control."

Many of the reports led to questions and discussions. The Conference adopted a resolution noting the achievements and gaps in the analysis of noble metals during the last two-and-a-half years; the Conference indicated what further work should be carried out in this field.

The Conference adopted a resolution to the effect that the reports should be published as soon as possible.

O.E. Zviagintsev

SYMPOSIUM ON THE THEORY AND APPLICATION OF COMPLEXONS IN ANALYTICAL CHEMISTRY

A symposium on the theory and application of complexons in analytical chemistry was held in Moscow on November 28-30, 1957. The symposium was convened by the Commission on Analytical Chemistry of the V.I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR,in accordance with the wishes expressed a year previously at the All-Union Conference on the application of organic reagents in analytical chemistry. More than 50 specialists in the field of complexometry participated in the symposium; these included representatives from the social democracies: R. Pribil and I. Kerbl (Czechoslovakia), L. Erdei (Hungary), Lian Shi-Tsuan and Tsen In-Tsao (China), Tutundzhich (Yugoslavia) and others. Thirteen reports were read; some of the reports were devoted to theoretical questions – the thermodynamic stability of complexes, the effect of molecular structure on indicator color, etc. Some attention was given to the synthesis of new complexons and color indicators, and also to the application of complexons, in particular, the use of Complexon III, for the separation (for example, with the aid of ion-exchange chromatography) and determinations of elements.

The communication of K.B. Iatsimirskii (Ivanovo) dealt with the results of a thermochemical study of complex compounds. Complexonates differ from other complex compounds in that the formation of the former is weakly exothermic or even endothermic. The author attributes the stability of the complexes to a decrease in entropy of the system and, from the viewpoint of the chemical process, by the fact that during complex formation, there occurs liberation of water molecules from the hydrated layer of the cation, followed by disorientation of these molecules. It was pointed out that when using an indicator, the rate of formation of the complex should be borne in mind. Thus, indicators are not suitable for elements which react slowly.

Color indicators play an important role in complexometry. Metallochrome indicators of the phthalein series and two new indicators – glycinethymol blue and glycinecresol red – were discussed in the report by R. Pribil (Prague). The author showed that glycinethymol blue gives an intense color with copper at pH 5-6, which is of a deeper blue than that of the complex formed between copper and ammonia. During titration with Complexon III, the color of the solution changes from blue to lemon-yellow. This indicator can also be used successfully in photometry. The other indicator – glycinecresol red is also suitable for copper determination. The color changes from red to yellow in this case. The author also gave some results on the application of other indicators – nitroazobenzopyrocatechin and sulfoazopyrocatechin, aminopropionic acid derivatives, and glycinenaphthol violet. The author demonstrated some experiments on titration with the new indicators.

I. Kerbl (Prague) communicated some results of a study of metallochrome derivatives of amino acids, and on the mechanism of metallochromic indicators. The capacity of an organic compound to bind cations is attributed by the author to the structure of the molecule and to the deformation of the electronic layers of the cation. The appearance of a color is also possible in the case of cations in which the electronic layers are not deformed (e.g., colorless ions). One of I. Kerbl's reports was devoted to titration error in complexometry.

The use of certain new indicators in complexometry was the subject of the reports given by L. Erdei (Budapest) and I.M. Mustafin (Saratov). The new indicator variamine was dealt with in the first report. This indicator gives a color change on changing the ratio of the components in the system ferricyanide-ferrocyanide (at pH 5), and this in turn shifts on the appearance or disappearance of ions of zinc, lead and others during titration with ethylenediaminetetracetic acid. The author demonstrated a very effective experiment in which a chemiluminescent indicator – luminol and hydrogen peroxide – was used for the determination of copper. Luminol and hydrogen peroxide give a luminescence which becomes weaker on addition of copper. During titration of such a solution with Complexon III the copper is complexed and the luminescence intensity increases; determination of copper is based on this fact. I.M. Mustafin's report demonstrated the possibility of using phenolcarboxylic acids of the triphenylmethane series as complexonometric indicators. The author has used these indicators for the determination of a number of cations: Be^{2+}, Mg^{2+}, Al^{3+}, Ni^{2+}, VO^{2+} etc. The compounds formed thereby are readily soluble in water and have an intense blue color. Some of the colored compounds are destroyed by solutions of complexons. The author demonstrated some experiments in which the new indicators were used.

A report by R. Pribl dealt with the complexonometric determination of oxidizing and reducing materials. The author uses the indicator xylene orange for this purpose. The report demonstrated the possibility of carrying out direct titration of mercury, zinc, lead, cadmium, bismuth, indium, and also the possibility of determining gallium, iron, copper, uranium, vanadium, chromium, aluminum, and tin. Thus, for the determination of vanadium, the latter is reduced with excess ascorbic acid which is complexed with Complexon III, excess of the latter being then titrated with thorium in the presence of an indicator. The author indicated the possibility of a photometric determination or a qualitative detection of trivalent uranium by means of indicators with which uranium gives very stable complexes not suitable for titration.

The report of P.N. Palei (Moscow) was devoted to the reducing properties of Complexon III. He showed that in acid media, under the influence of an oxidizing agent, the molecule of Complexon III undergoes a breakdown in which four molecules of CO_2 are liberated. The author was of the opinion that it is the COOH groups that break down. The report contained examples of the reduction of plutonium, vanadium, and chromium by Complexon III.

Exploratory work in the synthesis of new complexons and the study of their behavior was the subject of R.P. Lastovskii's report (Moscow). The use of a new fluorescent complexon — tetracetic acid - acridine yellow — was described in this report. This complexon is very suitable for paper chromatography (for example, for the separation of barium and strontium from calcium and magnesium). The author has also synthesized hexamethylenetetracetic acid which can mask iron without masking nickel and cobalt; and also parafuchsinhexacetic acid by means of which lead can be determined as an impurity in the presence of titanium. The author demonstrated the possibility of carrying out a polarographic determination of neodymium, lanthanum, and gadolinium by means of this last complexon.

In the report by Lian Shi-Tsuan and Tsen In-Tsao (Peking), which was devoted to the possibility of using complexes of pyrocatechin with trivalent iron for the determination of fluorine, results were given of the discovery of two more complexes in addition to the three already known. The authors showed that in the pH range 4.2-10, fluorine does not decolorize the complexes of pyrocatechin with iron (III), i.e., these complexes are more stable than the complex $[FeF_6]^{3-}$. Over the range pH 2-4, however, the complex $[FeF_6]^{3-}$ is the most stable.

The application of complexons in ion exchange was dealt with in the report given by M.M. Seniavin (Moscow). The high complexing capacity of the complexons allows them to be used successfully for chromatographic separation, for example, of the alkali metals. The author pointed out an interesting characteristic of the complexons — their bifunctionality, i.e., their capacity to form complex compounds with a bond through an oxygen or nitrogen atom; separation of mixtures of the rare earths by using inhibitor ions is based on this fact.

Analytical methods in nonferrous metallurgy based on the use of Complexon III was the subject of Iu.Iu. Lur'e's report (Moscow). The author gave several examples of the advantages of complexometry over other titrimetric methods such as iodometric, chromatometric methods, etc. Complexon III has been used successfully for phase analysis.

In the discussion that followed, A.K. Babko suggested the addition of Complexon III for slowing down crystallization processes. Thus, zirconium phosphate in the presence of Complexon III precipitates slowly without trapping titanium; the precipitate is readily filtered.

I.P. Alimarin, I.V. Tananaev, V.I. Kuznetsov, A.K. Babko and N.P. Komar et al. took an active part in the symposium.

Similar conferences in which both Soviet and foreign scientists take part, in addition to establishing friendly contacts, can, to a significant extent, help in the solution of new problems in analytical chemistry.

A.A. Pozdniakov

CONFERENCE ON THE USE OF RADIOACTIVE ISOTOPES IN ANALYTICAL CHEMISTRY

An All-Union Conference organized by the Chemical Sciences Section of the USSR Academy of Sciences and the Commission on Analytical Chemistry of the V.I. Vernadskii Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, was held in Moscow on December 2-4, 1957; the Conference was devoted to questions connected with the use of radioactive isotopes in analytical chemistry.

More than 450 scientific workers and representatives of production organizations participated. In addition to Soviet research workers, many foreign scientists from several countries took part (England, Bulgaria, Hungary, China, Poland, Rumania, USA, Czechoslovakia, and Yugoslavia).

Fifty reports were read at the Conference, 26 of these being the subjects of discussion at the Conference.

The plenary session was opened by Academician A.P. Vinogradov who outlined the basic uses of radioactive isotopes in analytical chemistry. Academician A.P. Vinogradov emphasized that at the present moment the radioactive isotopes of most of the elements of the periodic system are in use in analytical practice, and that their use is becoming as commonplace as the classical methods of qualitative and quantitative analysis.

At the plenary session, the report of A.V. Nikolaev, A.A. Sorokina and A.S. Maslennikov on the use of radioactive isotopes for developing methods for the separation of the rare earths was read. In their report, I.P. Alimarin and G.N. Bilimovich gave results on the use of isotope dilution for the determination of certain rare elements. Using the radioisotopes Nb^{95}, Zr^{95} and Ta^{182} the authors have developed methods for separating tantalum from titanium, zirconium and niobium, and for determination of tantalum by the isotope dilution method. The methods have been checked on the analysis of rocks and alloys.

The report given by A.N. Ermakov, V.K. Beliaeva and I.N. Marov was devoted to the use of labelled atoms (Zr^{95} and Hf^{181}) for the study of complex formation of zirconium and hafnium with the oxalate ion by an anion-exchange method. Taking this as an example, and using anion-exchange resins, the possibility was demonstrated of calculating the stability constants of the complex compounds of multi-charged ions which form stable complexes in strongly acid media with weakly dissociating materials.

I.M. Korenman and F.R. Sheianova reported on the use of nonisotopic indicators for solving a number of analytical problems, and adduced a large amount of experimental data on radiometric titration. The authors also demonstrated the possibility of determining solubility by using nonisotopic indicators (tetrathiocyanomercuriates, nitrocobaltiates, etc.).

At one of the sectional sessions A.I. Kulak gave a report on the quantitative determination of microamounts of certain metals present as impurities in ferric oxide by a radioactivation method.

The report of V.B. Gaidadymov and L.I. Il'ina on the analysis of binary tantalum-niobium alloys by means of reflection (back-scattering) of β-rays, attracted special attention. This method permits analysis of samples in different physical forms: powders, moldings and plates; the experimental error does not exceed 0.5% absolute for tantalum contents ranging from 2 to 98%. An analysis takes three to five minutes.

The subject of G.S. Rozhavskii and I.E. Zimakov's report was multi-radioactive dilution for the determination of small amounts of impurities.

M.B. Neiman, V.E. Efremov and V.N. Panfilov reported on determination of alcohols by the isotope dilution method.

K.B. Iatsimirskii and E.N. Rosliakova discussed radiometric titration and the use of solutions of complex compounds of cobalt 60.

I.P. Alimarin, A.K. Babko, V.I. Kuznetsov, N.P. Komar', K.B. Iatsimirskii and others took an active part in the discussion of the reports.

Professor I.M. Kolthoff (USA) gave a report with a wealth of detail on the use of radioactive isotopes for the study of aging of crystalline precipitates.

A.K. Lavrukhina discussed some characteristics of the technique of radiochemical analysis. Isolation of some short-lived isotopes from complex mixtures was discussed in the report of V.P. Shvedov and L.I. Ivanova, while M.M. Seniavin reported on the use of radioactive isotopes in chromatography. On the basis of experimental work on the adsorption of ruthenium from solution onto ion-exchange resins (E.I. Il'enko, B.P. Nikol'skii and A.M. Trofimov), the authors suggested an original method for the quantitative extraction of ruthenium from solution. Other reports were heard with equal interest: a carbonate method for removing micro-amounts of uranium from weighable amounts of iron (I.E. Starik, F.E. Starik and A.N. Apollonova); a study of precipitation conditions in ternary systems: dye-base, metal, halogen (A.K. Babko and P.V. Marchenko); isolation of uranium from sea water by means of organic coprecipitants (V.I. Kuznetsov and T.G. Akimova); coprecipitation of certain elements at low concentrations of the latter with metal hydroxides (Iu.V. Morachevskii and A.I. Novikov).

At the last session G.I. Irving (England) reported on the analytical chemistry of indium. A report on the study of the analytical chemistry of francium by means of the radioactive isotope Fr^{212} was then read (A.K. Lavrukhina, S.S. Rodin). The report led to a lively discussion. In particular, K.B. Iatsimirskii pointed out the general rules relating the solubility of the alkali metals to the dimensions of the cation and the anion; N.B. Mikheev spoke on the isomorphism of the salts of cesium and francium with silicotungstic and phosphotungstic acids; V.I. Kuznetsov communicated some ideas on organic coprecipitants for francium; I.V. Tananaev suggested the use of a series of mixed ferrocyanides for coprecipitation of francium.

The following reports were also heard: the use of radioactive indicators for checking on methods of isolating niobium (Iu.I. Bykovskaia); a technique for using radioactive indicators for controlling the production of rare metals (A.A. Gridik and N.I. Marunina); the use of Ca^{45} for determination of nonmetallic inclusions in steel (M.I. Tsekhanskii, N.I. Shishkina, K.V. Khusnoiarov and G.D. Susloparov); the use of Cl^{36} for the quantitative determination of hexachlorocyclohexane isomers in technical hexachlorane (P.V. Zimakov and L.A. Krasnousov); the use of labelled atoms for determination of the efficiency of fractionation of gaseous hydrocarbons (K.I. Karasev).

In his concluding remarks A.P. Vinogradov noted that analytical chemistry is, at present, a very important user of radioactive isotopes for the solution of many chemical questions. It is hoped, in the not too distant future, to discuss questions related to the apparatus and to the dosimetry of various types of radiation which are applicable to analytical chemical problems.

A.N. Ermakov

CRITICISM AND BIBLIOGRAPHY

"The Bases of Qualitative Chemical Analysis," N.I. Komar'. The A.M. Gor'ky Kharkov State University Press, 1955. Printing 10,000. Price 10 rubles 50 kopecks.

The book under review is a theoretical introduction to a course of qualitative chemical analysis.

The book consists of 19 chapters in which are set forth:

1. A brief account of the history of analytical chemistry in Russia;

2. Necessary information on the theory of solution and precipitation of sparingly soluble materials;

3. The application of the law of mass action to ionic equilibria;

4. The theory and practice of the application of organic reagents in chemical analysis;

5. The sensitivity of chemical reactions.

The book contains about 100 systematically chosen examples illustrating the application of the theory of ionic equilibrium in chemical analysis. The appendix contains tables of constants for calculating equilibrium during precipitation, complex-formation, oxidation, reduction, and other chemical reactions.

The book is the result of the penetrating, creative, and scientific research work of the author in the theory of analytical chemistry.

All the questions discussed are set forth at a high theoretical level and are successfully illustrated by numerical problems which certainly help in assimilating the material set forth.

Deserving of particular attention are Chapters XI, XIII and XV devoted to precipitation of sparingly soluble materials under conditions of supersaturation and heterogeneous equilibrium. By making use of a number of actual examples, the author has shown with perfect clearness and mathematical accuracy that the well-known equation of so-called relative supersaturation is of very limited application. The thermodynamic equation of V. Thomson which takes into account many individual properties of sparingly soluble materials (surface tension, molecular weight, density, crystal radius) permits a more accurate characterization of precipitation from homogeneous solutions.

A superficial acquaintance with the book gives the impression that it is overloaded with calculating material. But a more thorough study of the book dispels this impression: the successfully chosen and, from a mathematical point of view, reproachless examples from various branches of chemical analysis disclose the essence of the chemical processes which occur in aqueous solutions, and allow one to make a conscious choice of the conditions to be used in chemical experiments.

All the same, some of the chapters in the book under review do not contain an exhaustive exposition of the material. This is true of Chapter VI "Indicator Theory," and Chapter XIV, in the section on coprecipitation.

Bearing in mind that the book is designed for students in the second course in chemical faculties in state universities, during a study of qualitative analysis, a full discussion of these questions should be related to the course of quantitative analysis.

The scientific-theoretical level of the book leads one to express the opinion that it would be more suitably called "The Theoretical Bases of Chemical Analysis."

This book is a very valuable original textbook on the theory of analytical chemistry, important to both Russian and foreign literature, and will undoubtedly play a very essential part in preparing specialists in chemistry in state universities; it should become a bench book for research chemists.

A. Tikhonov

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THE ORGANIZING COMMITTEE OF THE EIGHTH MENDELEEV CONFERENCE ON GENERAL AND APPLIED CHEMISTRY

INFORMATION

The Organizing Committee of the Eighth Mendeleev Conference wishes to inform all chemists in the Soviet Union that on the 8-13th of December, 1958, there will be held in Moscow the Eighth Mendeleev Conference on General and Applied Chemistry.

In addition to plenary sessions at which communications will be read on the basic problems of modern chemistry, reports will also be heard and discussed on the following sections: 1) inorganic chemistry and technology (including rare elements); 2) organic chemistry and technology; 3) analytical chemistry; 4) physical chemistry; 5) colloid chemistry; 6) chemistry and technology of polymers; 7) chemistry of natural compounds and biochemistry; 8) agronomic chemistry; 9) chemistry and chemical technology of fuel; 10) chemistry and technology of food-stuffs; 11) chemistry and technology of silicates; 12) radiochemistry and the chemistry of isotopes; 13) theoretical and applied electrochemistry; 14) chemistry of metals and alloys; 15) the economics, planning, and organization of chemical production; 16) basic processes and apparatus of chemical technology; and 17) the history of chemistry and chemical technology.

In addition, a symposium will be held on advanced chemical education. The participants at the session will be delegates chosen by the individual branches of the D.I. Mendeleev All-Union Chemical Society, and those given a personal invitation by the Organizing Committee.

Others may take part in the conference, including young specialists and students by Guest Tickets.

Payment for personal expenses incurred by those coming from outside Moscow should be made by the institution or enterprise at which the given person works, or should be set down to the D.I. Mendeleev All-Union Chemical Society.

Participants may read one report.

The reports to be given at the session may be of two kinds:

a) reports containing new unpublished studies of a theoretical or experimental nature. In contrast to scientific communications read at conferences devoted to special topics, the reports to be read at the projected session should be of a more general character for science and practice. Not more than 15 minutes will be devoted to such reports;

b) brief communications – predominantly for young chemists – devoted to only new facts, new observations or theoretical ideas; five minutes will be devoted to this category.

Those wishing to read reports or brief communications at the session should inform the Organizing Committee of their intention and should send a signed report and forms not later than April 15, 1958 (Moscow, V-49, P/Ia 3085).

The report should only be printed on one side of the paper; two copies should be sent and the text should not occupy more than three typewritten pages – double spacing – including tables or drawings. Texts requiring complicated type setting should be avoided.

The report should be recommended by a scientific or educational establishment, an industrial enterprise, or by a branch of the All-Union Chemical Society. The report should be sent to the Organizing Committee under the signature of the head of the institution or establishment concerned. Reports accepted by the Committee will be published prior to the session.

Inquiries of a general nature should be sent to the following address: Moscow V-71, Leninskii Prospect, Chemical Sciences Section of the USSR Academy of Sciences, Chief Scientific Secretary of the Organizing Committee of the Mendeleev Conference, Professor V.V. Kozlov.

Organizing Committee of the Eighth
Mendeleev Conference

USSR ACADEMY OF SCIENCES

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

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The exceptional significance of dithizone, diethyldithiocarbamates, and other sulfur-containing reagents for analytical chemistry justifies the search for new sulfur-containing reagents. We have made a study of 8-mercaptoquinoline – the sulfur-containing analog of 8-hydroxyquinoline – as an analytical reagent. 8-Mercaptoquinoline has already been described long ago [1]; it has not yet been investigated as an analytical reagent, if one does not take into account one published article [2], the authors of which concluded that 8-mercaptoquinoline is of no interest from the viewpoint of analytical chemistry. 8-Mercaptoquinoline has attracted little attention from analysts, probably because of the difficultyof synthesizing it, and the poor keeping quality of its preparations which oxidize rapidly in the air. Since, however, one of us has developed a method of synthesizing 8-mercaptoquinoline [3], it has ceased to be available only with difficulty, while the discovery of the complete stability of the hydrochloride of 8-mercaptoquinoline in air has enabled 8-mercaptoquinoline to be kept in the form of this salt no less successfully than other sulfur-containing reagents.

On the basis of theoretical considerations advanced in [4], one can expect 8-mercaptoquinoline to exhibit the following properties:

a) This reagent should interact with elements of the hydrogen sulfide and ammonium sulfide groups, since the compounds formed by this reagent with the metals of these two groups contain a bond between the metal atom and sulfur, the tendency to whose formation is very characteristic for the elements of these two groups [4, 5].

b) 8-Mercaptoquinoline should react particularly energetically with those elements for which the existence of a clearly defined tendency to formation of stable sulfides and stable ammoniates is characteristic.

c) 8-Mercaptoquinoline should interact with the elements of the groups indicated, in more acid solutions than 8-hydroxyquinoline, since formation of sulfides proceeds in more acid solutions than formation of the hydroxides of these metals, the tendency to whose formation is reflected in the interaction of the elements with 8-hydroxyquinoline.

d) The complexes formed by 8-mercaptoquinoline, at least those complexes possessing normal composition, should be capable of extraction from aqueous suspensions by organic solvents which are immiscible with water. This should follow because of the binding (blocking) of the salt- and complex-forming groups of the molecules of 8-mercaptoquinoline by the atoms of the elements, since this blocking deprives the molecules of the reagent of their hydrophilic character and, in the absence of other interfering factors, enables the complex to be extracted completely [6].

e) 8-Mercaptoquinoline complexes should be colored. This follows from the fact that almost all compounds formed between metals and sulfur possess a chromophoric action and donate a color to those compounds into whose composition they enter [7]. In addition, these complexes contain the chromophoric combination Me – N.

By analogy with 8-hydroxyquinoline complexes, the possibility is not excluded in the case of 8-mercaptoquinoline complexes that the color intensity will increase as well, because of the presence of inner-molecular dissociation [8].

The study we have made of the analytical application of 8-mercaptoquinoline – preliminary results of which have been published earlier [9] – has shown that all the forecasts made above can be shown to be true. This clearly demonstrates once again the correctness of modern ideas regarding the mechanism of the reactions of organic reagents, and permits one with greater certainty on the basis of theoretical considerations, to indicate what will be the most interesting practical applications of any particular organic reagent. This facilitates experimental studies on the search for and study of new organic reagents.

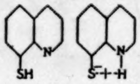
The Properties of 8-Mercaptoquinoline

Free 8-mercaptoquinoline (1) possesses totally different physical properties according to whether it contains water or is anhydrous.

Anhydrous 8-mercaptoquinoline C_9H_7NS is an intense blue colored liquid: on addition of water and, on even on storage in damp air, the material changes to a solid, red dihydrate. It is soluble in pyridine, quinoline, and ether, to give blue colored solutions, while in benzene and toluene the solutions are brown in color.

The reason for such a sharp difference between the colors of the anhydrous compound and the hydrate is not yet completely clear. The following is a possible explanation.

Many thioketo compounds containing aromatic nuclei are intensely colored. Thiobenzophenone [10], dithiobenzoic acid [11], and many of their analogs [12], just like anhydrous 8-mercaptoquinoline have a blue or blue-violet color. Since acid properties are fairly well pronounced in the thiophenols, free, anhydrous 8-mercaptoquinoline can be regarded as a partly inner-molecularly ionized compound (II). In this inner salt hydrogen is displaced toward the nitrogen, accordingly, the state of the sulfur approximates to its state in the intensely colored thioketo compounds. The blue color is the result.



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In the 8-mercaptoquinoline containing water, the groups $\diagdown N \diagup\!\!\!\diagup$ and −SH are blocked by the connecting molecules of water and, accordingly, the state giving rise to the blue color does not develop. Formation of an inner salt can also be excluded by substitution of the hydrogen in the −SH group by an alkyl group. Consequently S-ethyl-8-mercaptoquinoline is not blue but colorless.

In order to get inner complex salts of 8-mercaptoquinoline with a blue color, it would be necessary to have the salt of an element whose atom in the salt molecule would be strongly displaced toward the nitrogen atom and relatively far removed from the sulfur. In other words the element should possess a very strong tendency to form ammoniates and a relatively weak tendency to form sulfides. Ag, Cu, Ni, Zn, and the platinum metals form stable ammoniates. But Cu, Ag, and Zn to some extent, also form stable sulfides. This tendency is somewhat weaker in nickel and perhaps this is the reason the color of the nickel complex approximates to the color of anhydrous 8-mercaptoquinoline. The color of the nickel complex is not yellow like many other 8-mercaptoquinolates, but is raspberry.

The dihydrate $C_9H_7NS \cdot 2H_2O$ forms bright red needles, which on heating to about 58-59° split off water and change to the blue liquid, which was formerly taken to be the molten product [1].

In a vacuum, or on keeping in a desiccator over H_2SO_4, the elements of water are lost and the blue liquid is formed.

The solubility in 100 ml of water is 0.1 g (orange solution); the solubility in alcohol is about 12.5 g/100 ml (red solution). It dissolves in acids and alkalis to give yellow colored solutions.

In the solid state, and more rapidly in solution — particularly in alkalis — it is oxidized by atmospheric oxygen to the disulfide $C_9H_6NS \cdot SNC_9H_6$. It is stable in acid solutions.

The hydrochloride $C_9H_7NS \cdot HCl$ forms bright yellow crystals which are soluble in water, alcohol, and acetone acidified with hydrochloric acid, giving yellow colored solutions; it can be recrystallized from alcohol. It is insoluble in benzene. Both the solid material and its solutions are stable in air.

The sodium salt is fairly stable in the solid state in air but in aqueous solutions it is completely oxidized after a few days to the disulfide.

The disulfide of 8-mercaptoquinoline $C_9H_6NS \cdot SNC_9H_6$ is formed from 8-mercaptoquinoline by the action of an oxidizing agent, or by atmospheric oxygen in alkaline solutions; it is a bright yellow powder or crystals with a melting point of 206°. It is insoluble in water and alkalis, but dissolves in acids to give bright yellow colored solutions.

The analytical reactions of the disulfide are characterized by its capacity as a base to form sparingly soluble precipitates with a number of complex acids. Strong reducing agents (Ti^{III}, $Na_2S_2O_4$) change the disulfide to 8-mercaptoquinoline.

With solutions of the complex iodides of Bi, Sb, and Hg, the disulfide gives bright red precipitates, the formation of which is an interesting color reaction for these elements. Most of the other heavy anions form yellow precipitates.

The disulfide forms a dark brown precipitate with univalent copper, while with $SnCl_2$ it gives a yellow precipitate.

The Analytical Reactions of 8-Mercaptoquinoline

Precipitation of the Elements. The elements are precipitated by addition of an aqueous solution of 8-mercaptoquinoline hydrochloride to the test solutions; amorphous or granular precipitates are formed. By carrying out precipitation in a medium containing 30-40% of alcohol, many of the precipitates can be obtained in a crystalline form.

As a reagent forming the bond Me—S, 8-mercaptoquinoline precipitates elements of the hydrogen sulfide and ammonium sulfide groups, and particularly energetically precipitates elements which, in addition to forming Me—S bonds, also give stable bonds with amine nitrogen. Some elements are precipitated from solutions with a high acid content. The corresponding qualitative reactions are distinguished by high sensitivity.

8-Mercaptoquinoline, like 8-hydroxyquinoline, is a group reagent; this however does not prevent its use for carrying out various separations and determinations of different elements by adopting suitable conditions. The conditions and procedures followed in the case of these two reagents are, of course, different.

The new reagent, like 8-hydroxyquinoline, precipitates a number of elements in the form of compounds with a definite composition; and these compounds can, after drying, be weighed as such. Many of the compounds formed are readily soluble in organic solvents and can be extracted; this fact permits separation of insignificant amounts of certain elements from a large amount of other elements which do not react, and various separations can be carried out. In their capacity to be extracted by and to dissolve in organic solvents, the 8-mercaptoquinolates, in general, are better than the 8-hydroxyquinolates. Some 8-mercaptoquinolates in nonaqueous solutions form intensely colored solutions, so that photometric determinations become possible. With respect to the sensitivity of such reactions, 8-mercaptoquinoline is superior to 8-hydroxyquinoline and is similar to dithizone; 8-mercaptoquinoline, however, possesses better selectivity than dithizone.

By using 8-mercaptoquinoline, titrimetric determinations are also possible for a number of elements, which are based on the capacity of 8-mercaptoquinoline to change over smoothly into the disulfide under the action of an oxidizing agent.

8-Mercaptoquinoline differs from 8-hydroxyquinoline in that it exhibits a more clearly defined capacity to form sparingly soluble salts with acids which have heavy complex anions.

Some elements, depending on the conditions used, are capable of forming two different compounds. One compound is a typical inner-complex compound, while the other is the normal salt of the cation of 8-mercapto-

TABLE 1

Precipitation of Elements by 8-Mercaptoquinoline

Element	Conditions	Form and composition of the precipitate in the presence of excess reagent RH-C_9H_6NSH; R-C_9H_6NS	Notes
Ag	Acid medium	Bright red precipitate R–Ag · RH · · $3H_2O$	Formed, even in 24 N H_2SO_4
	" "	Yellow amorphous precipitate R–Ag	In the presence of excess Ag
	Ammoniacal	" "	
Cu^{II}	Acid, neutral, ammoniacal media	Brown precipitate $R_2Cu \cdot {}^1/_2H_2O$	Formed even in 4 N HCl and in 3 N NaOH
Au^{III}	Hydrochloric acid medium	Yellow crystalline precipitate $(RNHH)_3AuCl_6 \cdot H_2O$	
Zn	Acid, neutral, ammoniacal	Yellow amorphous precipate R_2Zn	
	Acid in the presence of SCN$^-$	Red precipitate $(RHH)_2 \cdot [Zn(SCN)_4]$	
Cd	Weakly acid, ammoniacal	Orange precipitate	In the presence of insufficient reagent – a yellow precipitate
Hg^{II}	Acid, neutral	Yellow amorphous precipitate R_2Hg	Formed even in 3 N HCl
Hg$_2^{II}$	Acid	Red-brown crystalline precipitate R–Hg · RH · $2H_2O$	
Tl^{I}, Tl^{III}	Weakly acetic	Yellow precipitate R–Tl	Tl^{III} reduced to Tl^{II}
Tl	Ammoniacal, alkaline	Yellow precipitate R–Tl	
Sn^{II}	Acid	Yellow amorphous precipitate	Composition variable
Sn^{IV}	Hydrochloric acid	Pale-yellow turbidity slowly develops	
Pb	Acid	Orange precipitate R_2Pb	
As^{III}	3 N HCl	Yellow crystalline precipitate $(RHH)_3$ $AsCl_6 \cdot 3H_2O$	
As^{V}	Hydrochloric acid	Yellow crystalline precipitate R_6As	Soluble in concentrated HCl
Sb^{III}	Acid in the presence of tartrates	Yellow fine crystalline precipitate $R_3Sb \cdot H_2O$	
	Alkaline in the presence of tartrates	No precipitate	
	Strongly hydrochloric	Orange precipitate	Sb is precipitated as the anion
	Strongly hydrochloric in presence of I$^-$		
Sb^{V}	Hydrochloric acid	Yellow fine crystalline precipitate $(RHH)_3$ $SbCl_6$	Sb^{V} converted to Sb^{III}
Bi	Alkaline in the presence of tartrates	Yellow amorphous precipitate R_3Bi	
V^{V}, V^{IV}	Acid	Light green precipitate R_2VO	V^{V} reduced to V^{IV}
Mo^{VI}	pH 2–3	Dark green precipitate $R_2MoO_2 \cdot H_2O$	
Mo^{VI}	Acid, on addition of $TiCl_3$	Light green precipitate	
W^{VI}	Acidification of alkaline solutions of tungstate-containing reagent	Dark green precipitate	
Mn^{II}	Alkaline in the presence of tartrates	Brown precipitate R_2Mn	
Fe^{III}, Fe^{II}	pH 5-6; alkaline in the presence of tartrates	Bright, red-brown precipitate R_2Fe · · H_2O	Fe^{III} reduced to Fe^{II}

TABLE 1 (continued)

Co^{II}	Weakly acid	Bright precipitate $R_2Co \cdot 2RH \cdot 2H_2O$	
Ni	pH 6-6.5, ammoniacal	Bright raspberry, rapidly darkening precipitate $R_2Ni \cdot H_2O$	
Pd	Strongly acid, neutral, alkaline	Red, fine crystalline precipitate $R_2Pd \cdot H_2O$	

quinoline with the complex anion of the element. For example, in hydrochloric acid solution in the absence of thiocyanates, zinc gives yellow $(C_9H_6NS)_2Zn$, while in the presence of thiocyanates it gives a red precipitate of $(C_9H_6NSH_2)_2 \cdot [Zn(SCN)_4]$.

A drawback of 8-mercaptoquinoline is its tendency to be oxidized to the disulfide by atmospheric oxygen. All the same, in acid solutions, this process is so slow that it does not present any difficulties during the analytical application of the new reagent.

Details of the analytical application of 8-mercaptoquinoline for the determination of various elements will be given in subsequent articles. The present article only deals with its analytical reactions in the very broadest sense. The behavior of 8-mercaptoquinoline toward a series of elements under various conditions, the behavior, and appearance of the precipitates formed, are described in Table 1.

The Solubility of Precipitates in Organic Solvents. Bromobenzene, bromoform, benzene, and toluene are particularly good solvents for precipitates of the 8-mercaptoquinolates.

Precipitates formed by the following elements are readily soluble in organic solvents: Cu, Zn, Hg_2^{II}, Tl, Sn^{II}, Pb, As^{III}, As^{V}, Sb^{III}, Bi, V, Mo, Mn, Fe, Co, Ni, Pd.

Precipitates formed by Au, Cd, and W are less soluble; while the precipitates formed by Ag and Hg^{II} are soluble only in pyridine and quinoline.

All solutions in nonaqueous solvents are colored. The most intensely colored solutions (brown) are given by the precipitates formed by Mn, Fe, Cu, and Co; Mo (green) and Ni, Pd, Os, Pt (red) give less intensely colored solutions. A number of elements – Zn, Hg, Bi, Sb, As, Pb, and Tl – give relatively weak-yellow colored solutions.

Table 2 contains the values for the molar extinction coefficients of solutions of the 8-mercaptoquinolates of certain elements.

The capacity of many 8-mercaptoquinolates to be extracted is strongly dependent on the pH of the medium. The pH ranges within which complete extraction of the 8-mercaptoquinolates of individual elements is possible are given in Figs. 1 and 2, while in Fig. 3 is shown the position of the extracted elements in the Periodic System.

TABLE 2

Molar Extinction Coefficients of Solutions of Certain 8-Mercaptoquinolates (Room temperature)

Element	E_{mole}	λ_{max}, mμ	Solvent
Mn	7000	413	Chloroform
Pd	7750	485	"
Fe	7000	444	"
Cu	7530	431	"
V	7400	412	"

The Possible Analytical Applications of 8-Mercaptoquinoline. 8-Mercaptoquinoline permits determination of small amounts of elements. The reactions of 8-mercaptoquinoline supplement or , in some instances, successfully replace those given by dithizone. The fact that the capacity of certain 8-mercaptoquinolates to be extracted by a solvent is strongly dependent on the pH of the medium means that clear-cut extraction separation of a number of elements is possible. It is important to note that the extraction of a number of elements proceeds readily from solutions containing large amounts of energetic masking-complexing agents; this means that it should be possible to determine small amounts of certain elements on a background of large amounts of other elements. Thus, extraction of iron (II) at pH 6.5 is possible in the presence of very large amounts of tartrates, oxalates, citrates, phosphates, fluorides, and thiocyanates.

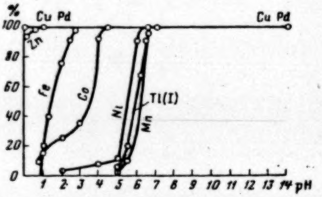

Fig. 1. Relation between the completeness of extraction of the 8-mercaptoquinolates of copper, palladium, zinc, iron, cobalt, nickel, thallium (I), and manganese, and the pH.

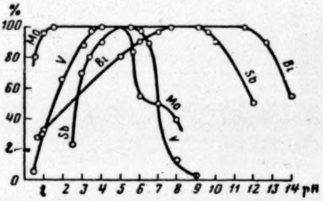

Fig. 2. Relation between the completeness of extraction of the 8-mercaptoquinolates of molybdenum, vanadium, antimony, and bismuth, and the pH.

Because of the intensity of the colors of the solutions of many of the metallic 8-mercaptoquinolates, direct photometric determinations of these elements is possible. The new reagent can, however, also be used for separation of elements with subsequent determination of individual elements by some other method; it is suitable as a component of organic coprecipitants and for amperometric titration.

H							
Li	Be	B	C	N	O	F	
Na	Mg	Al	S	P	S	Cl	
K □ Cu	Ca □ Zn	Sc □ Ga	Ti Ge	○ V ○ As	Cr ○ Se	Mn Br	○ Fe ○ C ○ Ni
Rb □ Ag	Sr □ Cd	Y □ In	Zr □ Sn	Nb ○ Sb	□ Mo ○ Te	I	□ Ru ○ Rh □ Pd
Cs □ Au	Ba □ Hg	La ○ Tl	Hf ○ Pb	Ta ○ Bi	□ W Po	Re	□ Os ○ Ir □ Pt
	Ra	Ac	Th	Pa	U		

Fig. 3. Extraction of elements by 8-mercaptoquinoline: □) extracted from strong acid solutions; ○) extracted from weakly acid and neutral solutions.

8-Mercaptoquinoline can also find application for precipitating and extracting a series of elements from very acid solutions, a fact which may be significant in certain cases. In this connection, 8-mercaptoquinoline, from the point of view of convenience of application and the results obtained, is better than thionalide (β-naphthalide of thioglycolic acid).

The disulfide, which does not form inner-complex salts, is capable of being converted by reducing agents to the active 8-mercaptoquinoline, which means that it is possible to carry out a number of interesting analytical determinations in combination with reduction.

The stability of 8-mercaptoquinoline toward even the strongest reducing agents suggests that by making use of it, it should be possible to apply the complexes of the lower valency states of a number of elements (Mo, W, etc) for analytical purposes, something which is not possible when dithizone is used.

SUMMARY

Analytical reactions of 8-mercaptoquinoline are described which are useful for the extractive separation of elements, and for the extractive photometric determination of very small amounts of a number of elements. The sensitivity of the reactions given by this new reagent is similar to that for dithizone reactions. From the point of view of convenience of application, and analytical possibilities, 8-mercaptoquinoline has a number of advantages over dithizone and thionalide.

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PHOTOMETRIC DETERMINATION OF THORIUM WITH ARSENAZO IN THE PRESENCE OF ZIRCONIUM, TITANIUM, AND THE RARE EARTHS

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The reagent arsenazo (uranon, benzene-2-arsonic acid –⟨1-azo-7⟩ dihydroxynaphthalene-3,6-disulfonic acid), suggested by Kuznetsov [1], is more sensitive toward thorium than other azochromotropic dyes such as thoron [2], chromazurol [3], carmine red [4], morelline [5], naphthizarin [6], and quinalizarin [7], but its selectivity is low. Zirconium, titanium, the rare earths, and also sulfate, fluoride, and phosphate ions, oxidizing agents, and other materials interfere with the photometric determination of thorium with arsenazo [1]. This explains the slow introduction of arsenazo into the chemical practice of production laboratories.

In the work described here we tried to increase the selectivity of arsenazo for the photometric determination of thorium, and sought for ways of eliminating interference from zirconium, titanium, and the rare earths.

Relation between the Optical Density of the Complex formed between Thorium and Arsenazo, and the pH of the Solution and Concentration of the Reagent. Aqueous solutions of arsenazo in weakly acid media have a rose color which changes to violet in the presence of thorium.

In our experiments we used a solution of thorium nitrate containing 19.34 γ Th/ml, and a 0.05% solution of arsenazo. Into 8 standard flasks with a capacity of 25 ml was introduced the solution of thorium nitrate containing 57.68 γ of thorium; 3 ml of the 0.05% arsenazo solution was then added; this was followed by 5% hydrochloric acid, or 5% sodium acetate, in such amounts that the pH of the solution, after making up with water to the mark, was 0.5-3.5. The optical density of the solution formed was measured (in these and subsequent experiments) on a photocolorimeter, in a 20 mm cell, using a yellow-green filter (572 mμ). The results obtained showed (Fig. 1) that the optical density of the solution is highest at pH 1.3-3.0. The color of the thorium complex reaches its maximum intensity when the concentration of the reagent is 1-1.5 mg in 25 ml (Fig. 2).

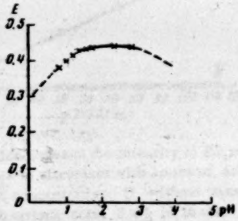

Fig. 1. Relation between the intensity of the color of the complex formed between arsenazo and thorium, and the pH.

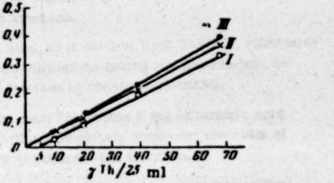

Fig. 2. Relation between the intensity of the color of the complex formed between arsenazo and thorium, and the amount of reagent: I) 0.25 mg arsenazo; II) 0.5 mg arsenazo; III) 1 and 15 mg arsenazo.

A Study of the Effect of Masking Agents on the Optical Density of Solutions of the Complexes formed between Arsenazo and Thorium and Zirconium. The color of solutions of the complex compound of zirconium with arsenazo is most intense at pH 1-2 [9]. The sensitivity of the reaction of thorium with arsenazo is equal to 0.7 γ/ml, while for zirconium it is about 0.1 γ/ml [9]. In the presence of even 5-10 γ of zirconium, determination of thorium is impossible.

Zirconium has a greater tendency to complex formation than thorium [8], and the complex compounds of zirconium are more stable than those of thorium. It is possible to choose compounds which would complex zirconium without touching thorium.

TABLE 1

Effect of Masking Agents on the Optical Density of Solutions of Complexes of Thorium and Zirconium with Arsenazo

5 mg of hydroxy acid added per 25 ml	Taken in, γ		Optical density	5 mg of hydroxy acid added per 25 ml	Taken in, γ		Optical density
	Th	Zn			Th	Zn	
	29	—	0.17	Sulfosalicylic acid			
Tartaric acid	29	—	0.17		29	—	0.14
"	29	30	0.17	"	29	30	0.30
"	—	30	0.01	"	—	30	0.15
"	—	30	0.15	"	—	30	0.15
Citric acid	29	—	0.14	Ascorbic acid	29	30	0.17
"	29	30	0.15	"	29	30	0.30
"	—	30	0.00	"	—	30	0.15
"	—	30	0.15	"	—	30	0.15

Table 1 contains results on the effect of various hydroxy acids on the color of the complex compounds of thorium and zirconium with arsenazo.

Tartaric acid does not depress the optical density of the solution of the complex of thorium with arsenazo; zirconium does not give a color, while in the absence of tartaric acid, the optical density of the solution of the complex of zirconium with arsenazo is equal to 0.15. When citric acid is used, the optical density of solutions of the complex of thorium with arsenazo drops from 0.17 to 0.14, although the effect of zirconium on the optical density of the thorium complex is not noticeable; in the absence of citric acid, the intensity of the color of solutions of the zirconium complex is also equal to 0.15. Sulfosalicylic acid does not mask zirconium but decreases the color appreciably. Ascorbic acid does not affect the color of solutions of complexes of thorium and zirconium with arsenazo.

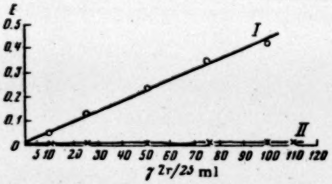

Fig. 3. Relation between the intensity of the color of the complex of zirconium with arsenazo, and the zirconium concentration: I) without tartaric acid; II) with tartaric acid; 5 mg in 25 ml.

Tartaric acid, as is evident from Table 1, eliminates interference from zirconium during the photometric determination of thorium by means of arsenazo.

It is clear from Fig. 3 that 5 mg of tartaric acid in 25 ml of solution completely suppresses the color of the complex of zirconium with arsenazo.

Table 2 contains results of measurements on the optical density of solutions of the complex of thorium with arsenazo, in the presence of various amounts of zirconium and tartaric acid.

From Table 2 it is clear that in the presence of 5 mg of tartaric acid in 25 ml of a solution containing 19.34 γ of thorium and up to 100 γ of zirconium, the optical density of the solution does not increase.

Zirconium, under the given conditions, does not interfere with the determination of thorium. In the presence of 10 mg tartaric acid, zirconium in amounts up to 150 γ does not interfere with the determination of thorium; when 30 mg of tartaric acid is used, zirconium does not interfere in amounts up to 300 γ; when 50 mg of tartaric acid is used, zirconium in amounts up to 700 γ (1:35) does not interfere with thorium determination. The optical density of solutions of the complex of thorium with arsenazo drops appreciably in the presence of 75-100 mg tartaric acid, so that determination of thorium is not feasible.

On the basis of these facts therefore, it is best to carry out determination of thorium by means of arsenazo in the presence of 50 mg tartaric acid in 25 ml of solution.

TABLE 2

Optical Density of Solutions of the Complex of Thorium with Arsenazo in the Presence of Zirconium and Tartaric Acid

Amount taken, in 25 ml			Optical density	Amount taken, in 25 ml			Optical density
$H_6C_4O_6$, in mg	Th γ	Zr γ		$H_6C_4O_6$, in mg	Th γ	Zr γ	
—	19.34	—	0.115	30.0	19.34	300	0.128
5.0	19.34	30.0	0.120	30.0	19.34	500	0.140
5.0	19.34	50.0	0.115	50.0	19.34	—	0.120
5.0	19.34	80.0	0.115	50.0	19.34	300.0	0.118
5.0	19.34	100.0	0.127	50.0	19.34	500.0	0.115
10.0	19.34	—	0.120	50.0	19.34	700.0	0.130
10.0	19.34	100.0	0.120	75.0	19.34	—	0.110
10.0	19.34	150.0	0.130	75.0	19.34	700.0	0.110
10.0	19.34	300.0	0.155	75.0	19.34	900.0	0.100
30.0	19.34	—	0.110	80.0	19.34	—	0.105
30.0	19.34	150	0.120	100.0	19.34	—	0.100
30.0	19.34	200	0.150				

Effect of Masking Agents on the Optical Density of Solutions of Thorium and Titanium Complexes with Arsenazo. Titanium, like zirconium, forms a colored complex with arsenazo and consequently interferes with the determination of thorium. The problem to be solved therefore was to eliminate interference from titanium during thorium determination. For this work a hydrochloric acid solution of titanium ($TiCl_6^{2-}$) was used; this solution was prepared as follows: 200 mg of titanium dioxide was fused in a porcelain crucible at 450-500° with 2.5 g of dry sodium peroxide. The cooled melt was dissolved in 200 ml of water and the whole boiled for 30 minutes. The solution was filtered and the precipitate on the filter washed 3-4 times with hot water; the titanium hydroxide was finally dissolved in 200 ml of hot 5% hydrochloric acid. Traces of hydrogen peroxide were removed by 1.0 N potassium permanganate. The titanium concentration was established by the cupferron method [10]. By diluting this stock solution with 5% hydrochloric acid, solutions of the requisite concentration were prepared.

Determination of thorium by means of arsenazo in the presence of titanium was studied using tartaric ($H_6C_4O_6$) and ascorbic ($C_6H_8O_6$) acids, as well as hydrogen peroxide.

Table 3 contains the results for determination of thorium in the presence of titanium, by means of arsenazo.

It is clear from Table 3 that up to 120 γ of titanium in 25 ml of solution does not affect the optical density of solutions of the complex of thorium with arsenazo. While the sensitivity of the reaction of thorium with arsenazo is equal to 0.07 γ/ml, that for titanium is only 5 γ/ml (i.e. 70 times less). The sensitivity of the reaction of titanium with arsenazo is even lower in the presence of 50 mg of tartaric acid; it is equal to 6 γ/ml. In the given instance, up to 150 γ titanium per 25 ml of solution (6 γ/ml) does not interfere during determination of thorium with arsenazo. Ascorbic acid also masks titanium; hydrogen peroxide depresses the optical density of solutions of the thorium arsenazo complex. Thus the use of tartaric and ascorbic acids ensures the photometric determination of thorium with arsenazo in the presence of considerable amounts of titanium (up to 8 γ/ml.)

TABLE 3

Effect of Titanium during Determination of Thorium with Arsenazo in the Presence of Complexing Agents

Am't contained in 25 ml sol'n			Optical density	Am't contained in 25 ml sol'n			Optical density
hydroxy acid in mg	Th γ	Ti γ		hydroxy acid in mg	Th γ	Ti γ	
—	19.34	—	0.165	$H_6C_4O_6$ 50	19.34	180.0	0.260
—	19.34	60.0	0.162	$C_6H_8O_6$ 10	19.34	180.0	0.165
—	19.34	120.0	0.160	$C_6H_8O_6$ 10	19.34	210.0	0.162
—	19.34	150.0	0.250	$C_6H_8O_6$ 10	19.34	240.0	0.300
$H_6C_4O_6$ 50	19.34	60.0	0.170	H_2O_2 30	19.34	—	0.140
$H_6C_4O_6$ 50	19.34	150.0	0.170	H_2O_2 30	19.34	60.0	0.140

Photometric Determination of Thorium in the Presence of the Rare Earths by Means of Arsenazo. The rare earths (total nitrates of the yttrium and cerium elements) in weakly acid or neutral media, just like thorium, form complex compounds of a blue-violet color with arsenazo [1]. The maximum color develops at pH 6-7; on decreasing the pH the color weakens and at pH 1-2 almost disappears.

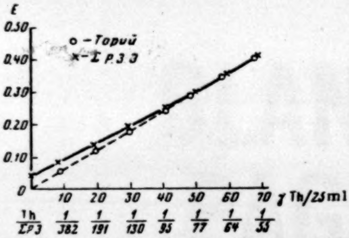

Fig. 4. Effect of the rare earths on the optical density of solutions of the complex of thorium with arsenazo (pH 1.3): O) Thorium; x) rare-earths

It is evident from Fig. 4 that at a ratio of thorium to the rare earths of 1 : 95 at a pH of 1.3, no deviation of the curve from the normal position (denoted by the dotted line) is observed. At higher ratios of the rare earths to thorium, the optical density of the solution decreases. When cerium is present it should be reduced to the trivalent state before carrying out photometric determinations of thorium with arsenazo. Ascorbic acid reduced Ce^{IV} to Ce^{III} in weakly acid media.

Tartaric acid in amounts of 50 mg per 25 ml of solution was also used in the next series of experiments as a masking agent.

Results for thorium determination in prêsence of various amounts of the rare earths are given in Table 4.

It follows from Table 4 that the rare earths, when present in amounts which are 900 times that of thorium, do not interfere with the photometric determination of the latter. In practice thorium could be determined at any concentration of the rare earths.

A Method for the Determination of Thorium in the Presence of Zirconium, Titanium, and the Rare Earths

An aliquot of the oxides of thorium, zirconium, titanium, and the rare earths* equal to 20-25 mg, is placed in a small porcelain crucible (1.5-2 ml), to which 0.2-0.3 g of dry sodium peroxide has been added beforehand. The aliquot is covered with 0.8-1.0 g of sodium peroxide and the mixture fused until a homogeneous melt is obtained; the crucible is cooled and transferred to a 100-ml beaker, 50-60 ml of water is added and the whole heated for 10-15 minutes. The crucible is withdrawn from the beaker and the solution filtered through a filter paper (white ribbon grade 6 cm). The hydroxides on the filter paper are washed 5-6 times with hot water; the filtrate and washings are discarded.

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* They are freed from the major amounts of titanium and zirconium by the oxalate method. Thorium, rare earths, and calcium are quantitatively removed as the oxalates when calcium is used as the collector. The oxalates may contain traces of zirconium and titanium.

TABLE 4

Determination of Thorium with Arsenazo in the Presence of the Rare Earths

Hydroxy acid in 25 ml, in mg	Amount taken		Th : Σrare earths	Optical density	Th found, in γ
	Th γ	Σrare earths, mg			
—	—	25	—	0.05	—
—	—	10	—	0.04	—
—	—	5	—	0.02	—
—	—	3	—	0.01	—
Tartaric acid 50 mg, ascorbic acid 10 mg	—	25	—	—	—
The same	29.00	4	1 : 150	0.170	29.0
"	29.00	8	1 : 250	0.165	28.5
"	29.00	10	1 : 300	0.165	28.5
"	29.00	20	1 : 700	0.170	29.0
"	29.00	25	1 : 900	0.165	28.5
"	9.67	3	1 : 300	0.080	9.5
"	9.67	5	1 : 520	0.060	9.5
"	19.34	5	1 : 250	0.110	18.5
"	19.34	10	1 : 520	0.120	19.5
"	9.67	—	—	0.060	9.5
"	19.34	—	—	0.110	18.5
"	29.00	—	—	0.170	29.0

The stem of the funnel containing the filter paper is inserted into a 25-50-ml standard flask; the hydroxides on the filter paper are dissolved in 5-10 ml of 5% hot (80-90°) hydrochloric acid, ammonia is then added dropwise until the hydroxides are precipitated. The hydroxides are dissolved in 2-3 drops of hydrochloric acid sp. gr. 1.12, and the filter paper is washed with 0.09 N hot hydrochloric acid until the amount of solution in the flask is about 20-40 ml respectively (according to whether a 25 or 50-ml flask is used in the first instance).

TABLE 5

Determination of Thorium by Means of Arsenazo in the Presence of Zirconium, Titanium, and the Rare Earths

Amount taken, in mg				Th found, in mg	Error in Th, in mg
Th	Zr	Ti	Σ rare earths		
0.006	0.080	—	10.0	0.005	−0.001
0.006	—	—	10.0	0.005	−0.001
0.006	0.080	—	10.0	0.006	0.000
0.019	0.200	0.060	20.0	0.019	0.000
0.019	0.200	0.090	20.0	0.019	0.000
0.019	0.200	0.120	20.0	0.020	+0.001
0.019	0.200	0.150	20.0	0.018	−0.001
0.019	0.200	0.180	20.0	0.019	0.000
0.019	0.200	0.210	20.0	0.020	+0.001
0.055	0.200	—	20.0	0.049	−0.006
0.055	0.200	—	20.0	0.060	+0.005
0.055	0.200	—	20.0	0.050	−0.005
0.110	0.300	—	20.0	0.115	+0.005
0.110	0.300	—	20.0	0.113	+0.003
0.110	0.300	—	20.0	0.112	+0.002
0.110	0.300	—	20.0	0.110	0.000
0.170	2.500	—	100.0	0.160	−0.010
0.170	2.500	—	100.0	0.170	0.000

1-2 ml of 1% ascorbic acid is added to the cooled solution and the whole thoroughly mixed. The solution is made up to the mark with 0.09 N hydrochloric acid, the whole mixed again, and the thorium determined.

For this purpose 5-20 ml of the test solution is measured into a 25-ml standard flask, 0.5 ml of 10% tartaric acid, and 3 ml of 0.05% arsenazo solution are then added, the volume is made up to the mark with 0.09 N hydrochloric acid and the solution mixed thoroughly. The optical density is measured on a photocolorimeter using a yellow-green filter (570-572 mμ) and 30 mm cells.

The amount of thorium is established by means of a calibration curve. The blank solution is an aqueous solution of arsenazo containing 3 ml of 0.05% arsenazo to 25 ml of 0.09 N hydrochloric acid.

It is clear from Table 5 that results for the determination of thorium in the presence of zirconium, titanium, and the rare earths are satisfactory.

SUMMARY

It has been established that interference from zirconium, titanium, and the rare earths during the photometric determination of thorium with arsenazo can be eliminated by means of tartaric acid. A method has been developed for the determination of thorium by means of arsenazo in the presence of the elements indicated.

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* Original Russian pagination. See C.B. Translation.

REMOVAL OF ETHYLENEDIAMINETETRACETIC ACID FROM SOLUTION BY OXIDATION

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Ethylenediaminetetracetic acid (Complexon II) and its disodium salt (Complexon III) are finding more and more applications in analytical chemistry and chemical industry [1-17].

When analyses are carried out, the need sometimes arises for removing the complexons from the test solution; for this purpose oxidative breakdown is the most convenient. The study of the oxidation of complexons is also of interest because of the possibility of the presence of oxidizing agents in certain test solutions.

Only the breakdown of ethylenediaminetetracetic acid by heating with chlorates in hydrochloric acid media is described in the literature [18]. There is a reference to the interaction of ethylenediaminetetracetic acid with hydrogen peroxide in the cold [19]. The considerable stability of the complexons to nitric acid has been noted in a number of papers, but quantitative data is not adduced.

We have studied the oxidation of ethylenediaminetetracetic acid by nitric acid, nitrous acid, and ammonium persulfate.

1. Preparation of Solutions. An aqueous solution of diammonium ethylenediaminetetracetate containing 100 mg/ml was prepared by dissolving the requisite amount of Complexon II purified by the method of Blaedel and Knight [20] in ammonia. The solution thus prepared was standardized by complexometric titration with standard magnesium sulfate, using chromogen black special, ET-00 (eriochrome black T) in the form of finely ground powder mixed with NaCl in the ratio 1 : 200 as indicator.

The ammoniacal buffer solution with pH about 10 was prepared by dissolving 70 g of NH_4Cl in 500 ml ammonia (d = 0.9) and diluting this solution to 1000 ml.

Only chemically pure grade chemicals were used for the work. All the solutions were made up in distilled water which had been passed through the cation exchange resin KU-2 in the sodium form.

The vessels used for the work were boiled in a 2% ammoniacal solution of Complexon II in order to avoid errors connected with washing out of cations from the glass [21].

2. Experimental Procedure. To a measured volume of Complexon II solution acidified with HNO_3 and contained in a 250-ml conical flask was added the oxidizing agent, and the volume of the solution made up to 100 ml.

The flask was fitted with a reflux condenser to avoid changes in volume during heating. 25-ml aliquots were taken from the solution and transferred to 250-ml conical flasks, the aliquots were then diluted to about 100 ml and the excess acid titrated with 2 N KOH using congo red as indicator. 2-3 ml of buffer solution was added to each aliquot, indicator was next added until a clear-cut blue color was obtained; the solution was finally titrated with 0.01 M $MgSO_4$ until the color started to change to red-violet. From the amount of $MgSO_4$ solution used up in the titration, the percentage decomposition of Complexon II was calculated.

EXPERIMENTAL RESULTS AND DISCUSSION

a) Oxidation of Complexon II by Nitric Acid. As the results given in Table 1 show, Complexon II is oxidized very slowly in the cold by nitric acid. Percentage breakdown increases with increasing contact time and acid concentration, and reaches an appreciable value (about 4%) on long contact with 4 N HNO_3.

In neutral media, without heating, the titer of the Complexon II solution did not change even in the presence of large amounts KNO_3.

TABLE 1

Oxidation of Complexon II (4 mg/ml) by Nitric Acid at Room Temperature

HNO_3 concentration, in mole/liter	Contact time, in hours	Oxidation of Complexon II, in %	HNO_3 concentration, in mole/liter	Contact time, in hours	Oxidation of Complexon II, in %
0.5	24	0.0	2.0	24	0.4
0.5	48	0.1	2.0	48	0.6
0.5	192	0.8	2.0	192	2.2
1.0	48	0.4	4.0	24	0.7
1.0	96	0.7	4.0	48	1.1
1.0	192	1.3	4.0	192	4.0

On boiling nitric acid solutions of Complexon II, oxidation speeds up considerably (Table 2), nevertheless, complete breakdown is not achieved even on prolonged boiling with 4 N HNO_3. In neutral solutions in the presence of KNO_3, Complexon II is oxidized very slowly on boiling.

Accordingly, nitric acid is not suitable for the quantitative removal of Complexon II. During complexometric titration even of hot solutions, the nitrate ion does not interfere, since titration is carried out rapidly and at low acidity (pH 1.7-13).

TABLE 2

Oxidation of Complexon II (4 mg/ml) by Nitric Acid on Boiling

Duration of boiling, in hours	HNO_3 concentration, in mole/liter	Breakdown of Complexon II, in %	Duration of boiling, in hours	HNO_3 concentration, in mole/liter	Breakdown of Complexon II, in %
0.5	0.5	2	0.5	2.0	11
1.0	0.5	4	1.0	2.0	17
2.0	0.5	7	2.0	2.0	37
4.0	0.5	15	4.0	2.0	50
0.5	1.0	6	0.5	4.0	14
1.0	1.0	11	1.0	4.0	18
2.0	1.0	20	2.0	4.0	34
4.0	1.0	28	4.0	4.0	63

b) Oxidation of Complexon II by Nitrous Acid. Nitrous acid oxidizes ethylenediaminetetracetic acid more actively than nitric acid. Table 3 contains the results of tests on the oxidation of a 0.4% solution of Complexon II during a 30-minute boil in 0.5 HNO_3 to which various amounts of $NaNO_2$ had been added.

With increasing amounts of sodium nitrite, initially there occurs an increase in the percentage oxidation of Complexon II, nevertheless, further increases in the amounts of nitrite have no effect on completeness of the oxidation. Increasing boiling time and the HNO_3 concentration do not lead to a 100% oxidation of Complexon II either. This can be explained by the rapid breakdown of sodium nitrite with liberation of nitrogen oxides. Consequently, in subsequent experiments, addition of $NaNO_2$ was continued in 1 g or 0.5 g portions per 100 ml of a 0.4% solution of Complexon II in 0.5 N HNO_3 every 30 or 60 minutes boiling time (Table 4).

In this way, by adding $NaNO_2$ in portions it is possible by boiling for 3 hours to achieve complete oxidation of ethylenediaminetetracetic acid. The concentration of the ethylenediaminetetracetic acid does not affect its oxidation by nitrous acid. Additions of 6 separate portions of 750 mg of $NaNO_2$ per 100 mg Complexon II (in the course of 3 hours at the boiling point) lead to complete breakdown of the complexon.

TABLE 3

Oxidation of Complexon II by Sodium Nitrite

Amount of $NaNO_2$, in g	Percentage breakdown of Complexon II, in %
0.2	35
0.5	46
1.0	60
2.0	60
4.0	60

TABLE 4

Oxidation of Complexon II on Addition of $NaNO_2$ in Portions

Duration of boiling, in min	Am't of $NaNO_2$ added, in g	Number of portions	Oxidation of Complexon II, in %
60	1.0	1	60
120	1.0	2	85
180	1.0	3	99.5
240	1.0	4	100
30	0.5	1	45
60	0.5	2	90
120	0.5	4	97,5
180	0.5	6	100

c) Oxidation of Complexon II by Ammonium Persulfate. Complexon II is oxidized very rapidly by ammonium persulfate in a weakly acid medium at the boiling point. Complete oxidation of 100 mg of Complexon II is achieved by adding 200 mg of $(NH_4)_2S_2O_8$ and boiling for 10-15 minutes; changes in acid concentration ranging from 0.1 N to 2 moles/liter do not appreciably affect oxidation of the complexon. Comlexon II concentration has no effect either.

For the rapid and complete breakdown of Complexon II therefore the following technique can be recommended.

To a solution of Complexon II acidified with HNO_3 is added an excess of ammonium persulfate (not less than twice the amount of the Complexon II in solution); the solution is heated to the boil and the temperature kept at this point for 10 minutes.

A drawback of this procedure is the formation of SO_4^{2-}, which sometimes interferes with the subsequent course of the analysis. In such cases another technique can be used.

To a nitric acid solution (0.5-1 N), sodium nitrite is added in small portions while the solution is being boiled. The amount of $NaNO_2$ added should be about 10 times the amount of Complexon II is solution.

SUMMARY

The percentage oxidation of Complexon II by nitric acid, nitrous acid, and ammonium persulfate has been studied. A technique has been developed for the rapid breakdown of Complexon II by ammonium persulfate and sodium nitrite.

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POLAROGRAPHIC CHARACTERISTICS OF THE THIOSEMICARBAZIDE COMPLEX OF COPPER IN SULFURIC AND HYDROCHLORIC SOLUTIONS

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The polarographic method has been successfully used for studying the complex compounds of many cations [1]. The chief condition for the applicability of the polarographic method for the determination of the instability constants of complexes [2] is the reversibility of the reduction of the ions on a dropping mercury cathode.

Every reversible electrode process is characterized by the fact that its only slow stage is the slow diffusion of ions to the electrode surface. The other stages of the electrode process are fairly rapid. The value of the electrode potential depends on the concentration of the ions located near the electrode surface.

The equation for the cathode wave in the case of reversible processes is of the following form:

$$E = E_{1/2} - \frac{0,059}{n} \log \frac{i}{i_d - i}.$$

In the case of irreversible electrode processes, the shift in potential of the half-wave is not directly related to the instability constant of the complex. This shift depends on the value of the exchange current and the discharge and ionization constants (α and β) [3]. Moreover, complexes with a different composition than those found in solution in the greatest amounts may be discharged.

The solutions were examined polarographically on a visual polarograph of the UFAN type (Ural Branch of the USSR Academy of Sciences). A saturated calomel electrode was used as the anode, this being connected to the electrolyzer via an agar-agar bridge with saturated potassium chloride. The cathode was a dropping mercury electrode. The dropping time was determined from the time of formation of a drop at the half-wave potential, for a constant value of the mercury column (τ = 1.01 seconds).

The value of m for the capillary was 1.57 mg/second. The capillary used had the following characteristic:

$$m^{2/3} \tau^{1/6} = 1.35 \text{ mg}^{2/3} \text{ second}^{-1/2}.$$

A mirror galvanometer with the following characteristics was used for measuring the current passing through the electrolyzer: R_{EN} = 398 ohm; $R_{crit.}$ = 1312 ohm. The oscillation period of the mirror was 16 seconds, and the sensitivity of 0.97×10^{-9} amperes/mm/m. All tests were carried out in a thermostat at a temperature of 25 ± 0.3°.

The solutions used were prepared from twice-distilled water. Cupric sulfate, potassium chloride, and thiosemicarbazide were twice recrystallized from the twice-distilled water.

The solution of thiosemicarbazide sulfate was prepared by dissolving an aliquot of the material in 2 N sulfuric acid, while that of the thiosemicarbazide chloride was prepared using 1 N hydrochloric acid. The copper concentration was 4×10^{-4} mole/liter, while that of the sulfate and chloride of thiosemicarbazide was $4 \times 10^{-3} - 4 \times 10^{-2}$ mole/liter.

The pH value — measured potentiometrically by means of a quinhydrone electrode — was equal to one for sulfuric acid solutions of copper thiosemicarbazide, and to zero for hydrochloric acid solutions.

Dissolved oxygen was removed from solution by passing hydrogen for 10-15 minutes through the solution; polarograms were then taken.

Corrections for the ohmic drop in the electrolyzer circuit were applied during determination of $E_{1/2}$.

The resistance of the electrolyzer we used had a value of 550-650 ohms. For a current strength of 10-20 μA, the correction for the ohmic drop in the electrolyzer circuit did not exceed 0.0065-0.0116 volt.

The polarographic wave for reduction of thallium ions on a dropping mercury electrode in a supporting electrolyte of 1 N KOH was taken first. The half-wave potential in the given case, according to [2], is equal to 0.475 volt. The value we obtained for the half-wave potential during reduction of thallium ions almost agreed with this, and was found to lie within the limits 0.476-0.481 volt.

In order to check on the reversibility of the reduction of copper thiosemicarbazide complex, the cathodic wave in a solution containing 4×10^{-4} mole/liter of Cu^{2+} in a supporting electrolyte of 2 N sulfuric acid (activity about 1) was taken. It is clear from Fig. 1 that reduction of cupric ions on a dropping mercury electrode using 2 N H_2SO_4 as supporting electrolyte proceeds in one stage: $Cu^{2+} + 2e \rightarrow Cu^0$.

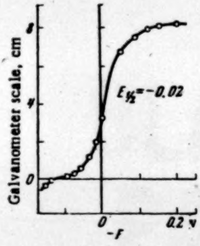

Fig. 1. Polarogram for a solution of cupric sulfate in 2 N sulfuric acid.

Polarograms were then taken for solutions containing cupric sulfate (4×10^{-4} mole/liter) and thiosemicarbazide. In Figs. 2a and 3 are shown the cathodic waves for reduction of the copper thiosemicarbazide complex.

The addition of thiosemicarbazide to the solution leads to a shift of the half-wave potential toward negative values (Figs. 2a and 3); this last fact indicates that a complex is formed between copper and thiosemicarbazide. The value of the half-wave potential for reduction of the copper thiosemicarbazide complex in a supporting electrolyte of 2 N sulfuric acid is -0.35 to -0.31 volt.

The curve in Fig. 2b, drawn within the coordinates E–logarithm $\frac{i}{i_d - i}$, testifies to the fact that one of the chief conditions for the reversibility of a given electrode process is not observed.

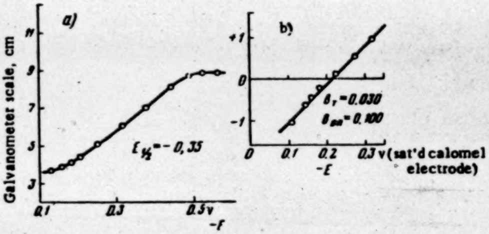

Fig. 2. Polarogram for a solution of the copper thiosemicarbazide complex in 2 N sulfuric acid as supporting electrolyte. Concentration of the thiosemicarbazide added 4.0×10^{-3} mole/liter.

The value of the tangent (for a copper concentration of 4 $\times 10^{-4}$ mole/liter and thiosemicarbazide concentration of 4 $\times 10^{-3}$ mole/liter) as found by calculation on the basis of several experiments ($\text{volt}_{\text{expt.}}$) proved to be 0.100, while the theoretical value of this coefficient ($\text{volt}_{\text{theor.}}$) corresponding to a reduction of Cu^{2+} to Cu^{0} is equal to 0.030.

Moreover, on increasing the thiosemicarbazide concentration 10 times (from 4 $\times 10^{-3}$ to 4 $\times 10^{-2}$ mole/liter), the half-wave potential of the copper complex shifts by 0.04 volt to more positive potential, from -0.35 to -0.31 volt. It is easy to see that if the process were reversible, this shift should be toward the negative side.

On this basis, it is possible to conclude that reduction of the copper thiosemicarbazide complex in sulfuric acid solutions belongs to the category of irreversible electrode processes and, consequently, it is impossible to determine the instability constant of the copper thiosemicarbazide complex polarographically.

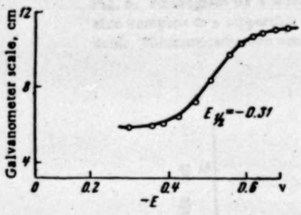

Fig. 3. Polarogram for a solution of copper thiosemicarbazide complex in 2 N sulfuric acid as supporting electrolyte. Thiosemicarbazide concentration 4.0 $\times 10^{-2}$ mole/liter.

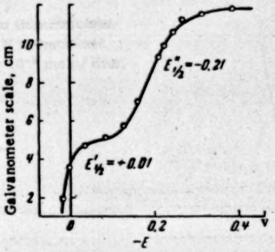

Fig. 4. Polarogram for a solution of cupric sulfate in 1 N hydrochloric acid as supporting electrolyte.

For the polarographic study of the copper thiosemicarbazide complex in a supporting electrolyte of hydrochloric acid, cathodic waves for Cu^{2+} in hydrochloric acid with an activity of about 1 (Fig. 4.) were again taken first; the solution contained 4 $\times 10^{-4}$ mole liter of copper. In this case, two waves were observed, one with a half-wave potential of +0.01 volt and the other with a half-wave potential of -0.21 volt; this is in accordance with published results: +0.04 volt and -0.22 volt for 1 M HCl (KCl) [4]. Cathodic waves were then taken for solutions containing cupric ions 4 $\times 10^{-4}$ mole/liter, and thiosemicarbazide 4 $\times 10^{-3}$ – 4 $\times 10^{-2}$ mole/liter in a supporting electrolyte of 1.0 N hydrochloric acid. The nature of the reduction of the complex ions of divalent copper in a hydrochloric acid solution of thiosemicarbazide can be followed by means of Figs. 5 and 6. It is clear from these diagrams that the discharge of the complex copper ions proceeds in two stages. The half-wave potential of the cathodic wave corresponding to the first stage of the discharge of the copper thiosemicarbazide complex shifts by 0.03 volt toward negative values, while the half-wave potential of the second stage shifts by 0.07 volt. It follows, therefore, that in a hydrochloric acid solution of thiosemicarbazide, complex copper ions are formed.

It is clear from Fig. 5 that the values of the half-wave potentials corresponding to reduction of the copper thiosemicarbazide complex in 1 N hydrochloric acid are equal to -0.02 and -0.28 volt.

A consideration of the curve constructed within the coordinates

$$E - \text{logarithm}\ \frac{i}{i_d - i}$$

(Fig. 5b) shows that the value of the tangent $v_{\text{expt.}}$ of the second stage of the discharge is equal to 0.100; it

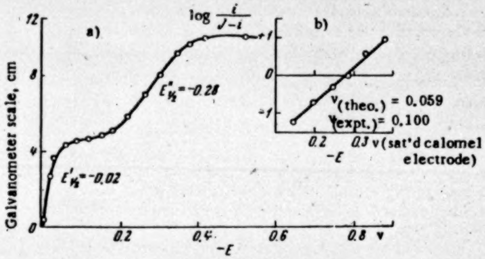

Fig. 5. Polarogram for a solution of the copper thiosemicarbazide complex in a supporting electrolyte of 1 N hydrochloric acid. Thiosemicarbazide concentration 4.0 x 10^{-3} mole/liter.

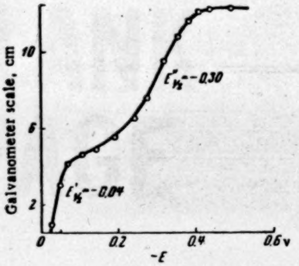

Fig. 6. Polarogram for the copper thiosemicarbazide complex in 1 N hydrochloric acid as supporting electrolyte. Thiosemicarbazide concentration 4.0 x 10^{-2} mole/liter.

is about one and a half times the theoretical value $v_{theor.}$ (0.059 at 25°); the process is accordingly irreversible. The tangent for the first stage of the discharge of the complex could not be calculated because it was impossible to determine the height of the first wave (i_d).

Preliminary experiments have shown that it is possible to determine copper polarographically in the form of its thiosemicarbazide complex.

We should like to thank A. G. Stromberg for his valuable advice.

SUMMARY

1. It has been established that the value of the half-wave potential for the cathodic reduction of the copper thiosemicarbazide complex in 2 N sulfuric acid as supporting electrolyte is equal to -0.31 to -0.35 volt (with respect to the saturated calomel electrode).

2. It has also been established that the values of the half-wave potential for the cathodic reduction of the copper thiosemicarbazide complex in 1 N hydrochloric acid as supporting electrolyte are 0.02-0.04 volt

and -0.28 to -0.30 volt, respectively, for the first and second stages.

3. It has been shown that reduction of the copper thiosemicarbazide complex on a dropping mercury electrode is irreversible in both sulfuric and hydrochloric acid as supporting electrolyte.

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HIGH-FREQUENCY TITRATION

COMMUNICATION IV. AN APPARATUS BASED ON A BRIDGE SETUP*

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The successful penetration of high-frequency alternating currents into chemical analysis and production control will be determined above all by whether or not the apparatus used is readily portable, simple in construction, and sensitive to concentration changes over a wide range of concentrations. The present article contains a description of an apparatus which will satisfy these requirements to a greater extent than the setup described by us previously [1, 2].

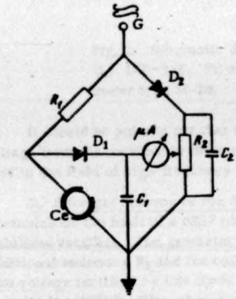

Fig. 1. Block diagram of the apparatus: G) high-frequency generator (35 megacycles; D_1, D_2) germanium detector DGTs6; Ce) titration cell; μA) microammeter.

1. Block Diagram of the Apparatus. When a cell for high-frequency titration is included in one of the arms of an ac measuring bridge, it is practically impossible to get a definite zero during balancing. This is explained by the appearance in the arms of the bridge of a shift in the voltage phase, and the appearance of additional harmonics (clear-factor) on the ends of the measuring diagonal. Complete elimination of these additional harmonics would complicate the setup considerably, since during balancing of the bridge it would be necessary to equate the voltage with respect to its modulus and phase simultaneously.** Accordingly, an ac bridge has not hitherto found application for high-frequency titration, and has only been partly used for measuring the concentrations of solutions over a narrow range of concentration changes with the help of calibration curves.

The bridge which we suggest in the present article is free from these drawbacks. In the apparatus described below, a high-frequency voltage is applied to the bridge, while the bridge is balanced on the basis of a dc current. Actually, as is clear from the block diagram, one of the branches of the bridge contains two resistances connected in series – an active resistance R_1 and the total resistance of the cell "Ce," while at the point where they join, a diode D_1 is applied; this diode rectifies the voltage across the cell. This rectified voltage is compensated by a constant voltage obtained by including a second

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*For Communication III see [11].

**For equilibrium of an ac bridge the following equation holds (in a complex form):

$$z_1 e^{j\varphi_1} z_3 e^{j\varphi_3} = z_2 e^{j\varphi_2} z_4 \cdot e^{j\varphi_4}, \qquad (1)$$

where z_1, z_2, z_3, and z_4 are the moduli of the total resistance of the bridge arms; $\varphi_1, \varphi_2, \varphi_3, \varphi_4$ are the voltage phases on these arms: [footnote cont.]

diode D_2 in the other branch of the bridge. Thus the zero reading of the galvanometer at balance is achieved without any of the complications connected with comparison of two constant voltages, as occurs in the usual four-arm dc bridge.

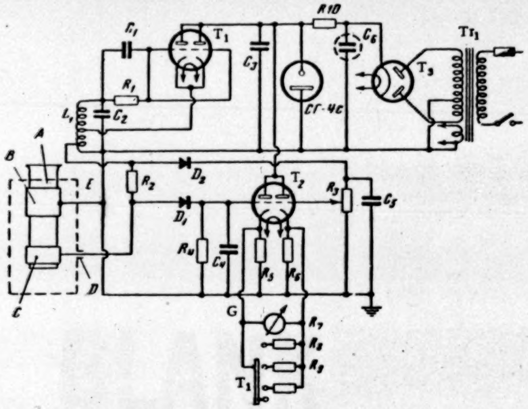

Fig. 2. Schematic diagram of the apparatus: T_1, T_2) 6N1P; T_3) 5TsChS; D_1, D_2) DG−Ts6; Tr) transformer; (ELS-2); A) cell (in a screen); G) μA-microammeter type M-24.

It should be pointed out that the principle of an ac bridge, but with a constant displacement of the voltage from the rectifier in the measuring diagonal, has been known for some time [4, 5] but has not been used in the field of high-frequency titration [6-8].

2. Principal Scheme of the Apparatus (Fig. 2). The high-frequency generator (35 megacycle was assembled on the basis of a 6N1P tube on the usual three-point scheme, the generator being supplied from a stabilized rectifier. The generator supplies two circuits simultaneously; one of these circuits consists of the additional resistance R_2 and the cell A. The voltage applied to the cell is rectified by the diode DG-Ts6. The voltage rectified by this diode proceeds from the load R_4 (with a blocked condenser C_4) to the grid of the first triode Li(6N1P). The other, the compensation circuit, fed by the generator, consists of a germanium diode D_2 (DGTs6), and a load R_3 with a blocked condenser C_5. Under these conditions, the compensating voltage

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••[Footnote continued from previous page] From (1) it follows that:

$$z_1 \cdot z_3 = z_2 \cdot z_4$$

$$\varphi_1 + \varphi_3 = \varphi_2 + \varphi_4 \qquad (2)$$

Equation (2) is a condition for the balance of an ac bridge; it should be balanced with respect to the moduli of resistance and voltage. To achieve this it would be necessary to introduce not less than two regulated parameters — active and capacitive resistance.

applied to the grid of the second arm of the triode T_1 can be regulated so as to obtain a null reading of the indicator galvanometer G.*

The galvanometer G is connected between equal cathode resistances R_5 and R_6, and is shunted by one of the resistances $R_7 - R_9$ for obtaining various limits for the measurements; by altering the shunt, it is possible to use 100, 80, 60, 40, and 20% of the maximum sensitivity of the apparatus; this permits titration to be carried out over a wide concentration range for the test solutions (10^{-3} N $-$ 5 x 10^{-1} N with respect to HCl).

The oscillating circuit L_1C_1 of the generator is calculated so that the frequency of the oscillations generated is equal to 35-40 megacycles. This frequency, in conjunction with the types of cells we used, permit work to be carried out with solutions with a high concentration (e.g. in the case of HCl, up to 5 x 10^{-1} N), since the capacitive resistance $X_{ct} = \frac{1}{w} C_{ct}$ between the lining and the solution is sufficiently small in this case [1].**

In order to line up the output resistance of the generator with the resistance of the cell circuit (i.e. in order to make more efficient use of the power supplied by the generator) the voltage in the cell circuit is taken from some of the windings of the induction coil L_1 of the oscillating circuit L_1C_2. The grid-leak C_1R_1 is included for the purpose of increasing the stability of the operation of the generator and its efficiency.

3. Construction of the Apparatus. The general appearance of the apparatus is shown in Fig. 3 ; its dimensiions are 215 x 105 x 214 mm. The transformer Tr (LS-2), the 5Ts4S tubes, SG-4S, the high-frequency generator (based on the tube 6N1P), the amplifier (based on tube 6N1P), and the other elements of the setup are mounted on the chassis of the apparatus. Two sockets are included in the left hand side of the chassis for connection with the cell block. The lower socket is a high-frequency "staker" connected with generator, while the upper socket is a metallic insert embedded directly in the wall of the housing ("ground connection").

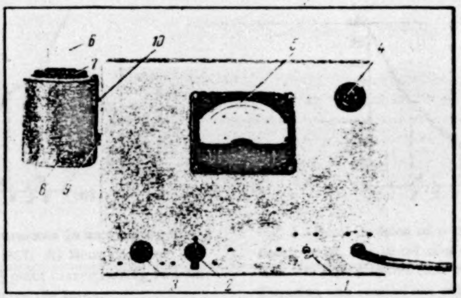

Fig. 3. General appearance of the apparatus.

The cell block consists of a thin-walled test tube 6 with two metallic bands wrapped round its outer walls (around its circumference). The test tube is mounted by means of rubber ring 7 in a metal screen 8 which has two brackets on its side wall; the lower one 9 is insulated from the body of the screen and is connected with the lower band on the test tube; the upper one 10 is embedded in the screen wall ("ground connection"), and is connected with the upper band on the test tube. By means of these two brackets, the cell in the screen is tightly packed into the appropriate socket on the side wall of the apparatus.

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*In the apparatus described earlier for high-frequency titration, compensation of the initial voltage was realized by galvanic elements [1, 2, 9]; as a result of this the readings of the apparatus depended to a very large extent on the grid voltage, since when the latter was used, the voltage across the cell changed while the compensating voltage remained constant. This limited the sensitivity of the apparatus and did not allow the use of an amplifier.

**Titration of concentrated solutions (of the order of 0.5–1 N) has been achieved by other authors by resorting to the use of the beat method [10] involving the use of a generator operating at a few hundred megacycles. This complicates the apparatus considerably.

A tumbler switch 1 is fitted onthe face panel of the apparatus for switching on the supply (from the network); onto this panel are also fitted the handle 3 of the potentiometer for adjusting the zero, the arm 2 of the throw-over switch for the shunting resistances, the signal lamp 4 and the microammeter for measuring the constant high-frequency current passing through the cell.

The apparatus is used as follows. After the cell with test solution has been inserted in position, the apparatus is switched on for 20 minutes before the start of a titration. Using 2, the optimum sensitivity for the given concentration is set. The microammeter needle is set to the beginning or end of the scale by means of 3, depending on the direction taken by the changes in the current during titration. The equivalence point is established graphically – by the intersection of the left and right branches of the titration curve [1].

4. Application. The apparatus assembled on the basis of the scheme outlined above can be used for solving various analytical problems which turn up in factory and research work. Express methods – which are at the same time fairly accurate–have been developed for the quantitative determination of phenols, cresols, inorganic and organic acids and bases in dark-colored solutions containing suspensions and emulsions of synthetic resins; methods have been suggested for the determination of the total acidity of mineral oils, and for the determination of acetic acid in mixtures with sulfuric acid, and in mixtures with acetic anhydride [11, 15].

Of considerable interest is a method for the determination of ammonia in aqueous suspensions of latex used in the rubber industry.* A known volume of the latex suspension is placed in the cell for high-frequency titration, and titrated with HCl with constant agitation. The first break on the titration curve corresponds to neutralization of ammonia (Fig. 4). The latex begins to coagulate at this point. The second break on the titration curve corresponds to completion of coagulation; at this point, the deposited latex sticks to the stirrer used for agitating the mixture. By means of this apparatus it is possible to carry out high-frequency titration in nonaqueous media, under conditions where a choice has been made of the most suitable solvent for the given purpose [12, 13].

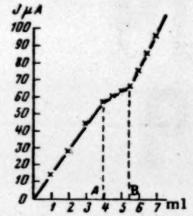

Fig. 4. Titration of ammonia in an aqueous suspension of latex with HCl: A) Neutralization point of ammonia; B) point corresponding to completion of coagulation of the latex.

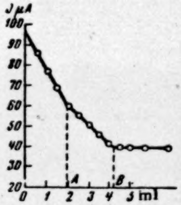

Fig. 5. Back titration of o-nitraniline in glacial acetic acid. To 10 ml of a solution of o-nitraniline was added excess (2.5 ml) 0.3865 N $HClO_4$. Titration was carried out with 0.2126 N CH_3COONa solution: A) Amount of sodium acetate used to titrate excess acid; B) amount of sodium acetate used to titrate o-nitraniline.

In Fig. 5 is shown the back-titration curve of o-nitraniline.** In this method, an excess of standard perchloric acid is added to a known volume of test solution in glacial acetic acid; high-frequency titration is then carried out in perchloric acid, using an acetic acid (anhydrous) solution of sodium acetate of known strength as titrant. This first break on the titration curve corresponds to excess $HClO_4$, while the second break corresponds to the content of o-nitraniline.

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* This work has been carried out by one of the authors in conjunction with V. N. Provorov and S. A. Nikitina (Institute of the Rubber Industry of the USSR Ministry of Chemical Industry).

** According to the results of A. A. Nemodruk and V. A. Frolkina.

According to preliminary results, by using the apparatus described in conjunction with a differential solvent [14] (acetone + water), it is possible to determine the equivalence point during titration of weak organic acids (or their total) of the type of ortho-, para-, or meta- chlorophenols by an aqueous acetone solution of NaOH.*

SUMMARY

A highly-sensitive, portable instrument has been developed for high-frequency titration; this apparatus is easy to construct and operate. By means of this apparatus it is possible to carry out titration over a wide concentration range ($0.5\ N - 1 \times 10^{-3}\ N$); it can also be used for studying various reactions in nonaqueous media.

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*According to the results of K. Kh. Arkhipova and R. F. Iliukhina.

**Original Russian pagination. See C.B. Translation.

***In Russian.

****Russian translation.

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A PHOTOGRAPHIC METHOD FOR MEASURING THE INTENSITY OF THE COLOR OF SOLUTIONS IN SMALL VOLUMES

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For the determination of very small amounts of materials, microspectrophotometry can be successfully used in addition to ultramicrochemical methods [1,2], since in the case of small volumes of solution, the amount of material necessary for analysis is very little (when one takes into account the sensitivity of the photometric method which allows one to operate with very dilute solutions).

There are published descriptions of a few types of cells which, in combination with photometers (in particular, the photoelectric spectrophotometer SF-4), can be used for measuring the intensity of the color of small volumes of solution [3, 4].

In the present article, which is devoted to work carried out in 1949, a description is given of a simple apparatus for a photographic method of measuring the intensity of colors of solutions in capillary cells which have a capacity of 0.05-0.1 ml.

The Principles of Operation of the Apparatus. The apparatus is shown schematically in Fig. 1. The test solution is poured into cell 1, while the other cell 2 is filled with solvent or a standard solution whose concentration should be less than the concentration of the test solution. Both cells are placed alongside each other in the path of a beam of light, directly in front of the photographic plate 3 arranged perpendicularly to the axis of the cell. After the photographic plate has been fixed in position it is possible to detect on it the images of the openings of both cells. For a given exposure, the intensity of blackening of the plate will depend on the brightness of the pencil of light passing through the cell; the blackening will be less, the higher the concentration of the solution. A continuous optical reducer (attenuator) 4 is placed in front of the reference cell 2; by shifting this reducer it is possible to find a position corresponding to equal blackening of both images. In such a case, it can be assumed that the absorption of the test solution is equal to the total absorption of the

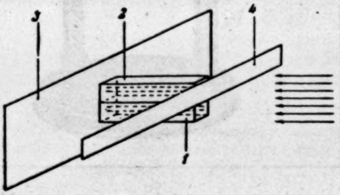

Fig. 1. Schematic diagram of the microcolorimeter. 1) Cell containing test solution; 2) cell containing standard solution; 3) photographic plate; 4) optical reducer (attenuator).

light by the standard solution (or solvent) and the corresponding part of the reducer. Using a series of solutions with known concentrations, a calibration curve is constructed for the given standard solution within the coordinates: concentration of solution – position of the reducer, denoting the place of equal blackening. Having filled the cell with test solution, and having established the position of the reducer at which equal blackening

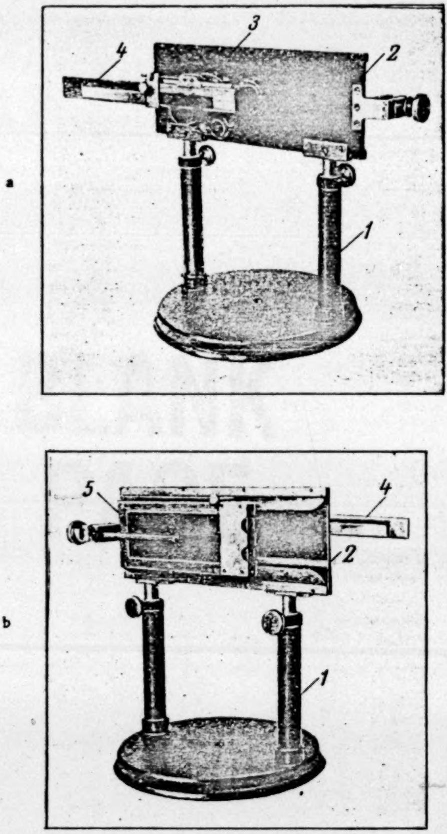

Fig. 2. General appearance of the microcolorimeter. a) Appearance from the front; b) from the back; 2) plate; 3) tube with shutter; 4) frame with attenuator; 5) cassette with photographic plate.

is obtained, the concentration of the test solution is then determined by means of the calibration curve. When the percentage reduction is known for each part of the reducer, then the concentration of the test solution can be calculated directly on the basis of Beer's law without resorting to the calibration curve.

Construction of the Apparatus. The general appearance of the apparatus is shown in Fig. 2. The apparatus consists of two parts - a lower, massive base 1 and the upper plate 2 fitted on it. On the front of the plate is located a tube 3 with a shutter in which there is a rectangular opening for the cell, and also a groove along which the frame, to which the optical attenuator 4 is fastened, moves. The attenuator is fixed so that it only darkens the upper cell; its position is fixed by means of a scale with a vernier.

On the back side of the plate there are longitudinal grooves along which, by means of a screw, the cassette 5 with the photographic plate (4.5 x 12 cm) is moved. For establishing the position of the cassette on the plate, a special scale is inscribed (as in an ordinary spectrograph).

Cell. The cell is illustrated in Fig. 3. It is made as follows. By means of a milling machine a groove about 1 mm deep is cut in the middle of a stainless steel plate (5 x 10 x 50 mm), the edges of the groove being made strictly parallel to the edges of the plate. Two small blocks, also of stainless steel and measuring (5 x 5 x 10 mm) are screwed into the steel plate at each end of the groove; they are screwed in along one of the 5 mm edges (see diagram). The ends of the plate and the corresponding surfaces of the blocks are ground parallel to one another and are polished. The shape of the openings at both ends of the cell should be exactly the same. Brass rings (diameter 10/7 mm, length 10 mm) are screwed into the end faces (or soldered with tin). A glass plate (10 x 40 mm) which covers the groove is accurately stuck onto the inner side of the cell by means of grease (e.g. picene). Before proceeding to fill the cell with solution, the opening at one of the ends is closed by means of a polished, plane, parallel, round window. For this purpose, the glass window is pressed onto the end surface by means of a small washer (diameter 7/3 mm, length 3 mm) with a slit for opening, screwed into the brass ring.

The cell can be filled in two ways depending on whether a large or small amount of solution is available. When the amount of solution is considerably in excess of 0.05 cm^3 (standard solutions, solvent, etc.), a glass tube can be used, having a diameter of 4-5 mm, whose end has been drawn out 70-80 mm to give an evenly cut opening with a diameter of 0.5-0.7 mm. Having taken up the solution in such a pipet and holding the cell in a horizontal position, the drawn out end is introduced into the cell so that it touches the bottom of the latter. By gradually inclining the cell, the solution is allowed to fill the cell slowly, taking care to see that no bubbles of air remain. During the filling process the pipet is gradually withdrawn from the cell, ensuring that the tip of the pipet is always immersed to a depth of 2-3 mm in the solution. When the cell has been filled, and the liquid meniscus is convex on the open side of the cell, the cell is sealed with the glass window, and the latter pressed home with the washer as indicated above. If there should be observed any bubbles of air, however small, on the walls of the cell, then the latter is shaken so that the bubbles accumulate at one of the ends, the window is then withdrawn, and a small amount of liquid added until a convex meniscus is formed; the end is finally sealed.

When the amount of liquid available is very small, then the cell should be filled under the microscope (x 25 - 30), using for this purpose a micropipet fitted with a piston attachment instead of the pipet described above; the construction of such a micropipet has been worked out and described by us previously [5]. The cell is fixed on a plate connected with the microscope stage so that the canal of the cell is in the field of vision; then by screwing the piston setup of the micropipet, the cell is filled as described above. The solution can be taken out of the cell by the same method.

Filling and emptying the cells are most important operations. It is essential that the glass windows be accurately and tightly fitted. If optical contact is not achieved then the solution will gradually evaporate, and bubbles of air may appear in the cell. For better hermetical sealing in such cases, the edges of the windows are smeared with a thin film of thick grease; care is taken during this operation that the grease is uniformly distributed in the form of a circle around the periphery of the windows, and that it does not extend beyond the openings of the cells. In order to avoid liberation of bubbles of dissolved air, it is recommended that the test solutions, etc. be heated to 40-50° before filling the cell.

A compensating setup may be used for obtaining a parallel beam of light, or the source of light may be set up at a long distance from the apparatus. We used the second variant. A 500 watt heating lamp set up at a distance of 5 meters from the apparatus was used as the light source.

The apparatus can be shifted and rotated during focussing; it is fairly stable, and the small forces associated with moving the cassette and the attenuator, and also with opening and closing the shutter do not affect its position. During focussing, the upper plate with the tube and cassette can be moved in a vertical position and can be fixed by means of screws.

Optical Attenuator. The continuous optical attenuator is a glass plate (15 x 180 mm), the blackening of which gradually increases on going from one end to the other of the plate. The preparation of a continuous attenuator by vacuum deposition of metal (usually plate metal) is in itself a fairly complicated problem. An attenuator can, however, be prepared in any laboratory from a piece of photographic plate as follows. An exposed, developed, and fixed photographic plate is placed in a vessel which is filled at a definite rate with a bleaching solution. By altering the rate at which the bleaching solution is poured in, it is possible to prepare an attenuator in which the blackening changes continuously. After bleaching the plate is fixed, washed, and dried. An attenuator could also be prepared by using a developer instead of a bleach, and treating the exposed photographic plate soaked in water. One should bear in mind that there is no linear relation between the bleaching time (and even more so, the developing time) and the blackening intensity, so that even for regular movement of liquid along the plate, the attenuators thus prepared are not linear. Moreover, the attenuators prepared in this way are not strictly grey. This, however, does not prevent them from being used in the method described. One of the cells is filled with standard solution, while the other is filled with test solution. Both cells are fitted together as shown in Fig. 3b (the position of one cell relative to the other is fixed by pins) and are placed in the rectangular opening of tube 3 of the apparatus (Fig. 2).

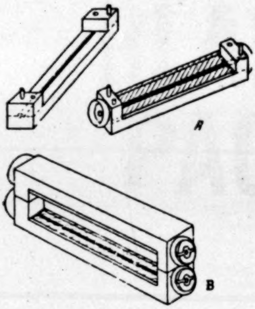

Fig. 3. Cell.

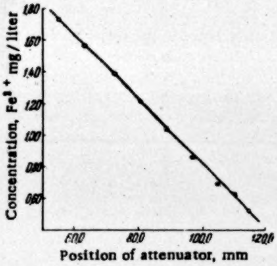

Fig. 4. Calibration curve.

Method of Measurement. The apparatus is set up in such a way that the cells are arranged on the level of the light source, while only one image of the incandescent filament can be seen through the opening. The correctness of the focussing is checked by means of a piece of frosted glass, the image of the opening on which should be sharp both for a small distance of the glass from the cell, and when this distance is increased to 5 - - 10 cm. By regulating the brightness of the lamp, the exposure at which normal blackening is obtained is established. The cassette plus photographic plate is placed in the apparatus and the shutter closed, after which 50 pairs of spots are photographed on the plate (at 2 mm intervals), while the attenuator and the cassette plus plate are moved. After development a pair of spots with equal blackening are sought for on the plate (visually, or by means of a microphotometer).

In order to establish more accurately the position of the attenuator corresponding to uniform blackening, the process of taking photographs may be repeated, the attenuator in this case being moved through shorter distances. The concentration of the solution is established by means of the calibration curve.

In order to increase the sensitivity of the method described, it is possible to use a light filter, the transmission region of which corresponds to the maximum absorption of light by the test solution. Naturally, when this is done, the concentration range which the given attenuator covers will be restricted. In those cases where it is desirable to extend the concentration range at the expense of the accuracy of the method, one can place a light filter which passes light in the region of weak absorption of the solution, in front of the cells. The conditions of work with white light is the mean of the two cases indicated. When a light filter is used, it should be borne in mind that the same one should be used both for constructing the calibration curve and for making measurements on the test solution.

The spectral sensitivity of the emulsion of a photographic plate has the same effect as the spectral characteristics of light filters; when the region of maximum sensitivity of the emulsion corresponds to the region of strong absorption of the solution, then the sensitivity will be increased, but the region of concentration covered by a given attenuator will decrease, and vice-versa. Accordingly, all measurements on the test solution should be carried out on photographic plates with the same kind of emulsion as that used for constructing the calibration curve (reproducing).

In Fig. 4 is shown, as an example, a calibration curve which we constructed for the quantitative determination of iron in the form of the colored complex of Fe^{3+} with o-phenanthroline. The concentration of iron in the test solutions varied over the limits $0.5 - 2 \times 10^{-3}$ g/liter. Accordingly, the amount of iron in the test solution (0.1 ml) amounted to $0.5 - 2 \times 10^{-7}$ g. Differences in the positions of the attenuator during replicate measurements carried out on the same solution, or on independently prepared solutions of the same concentration, did not exceed 0.5 mm; this corresponded to an error of $\pm 1 \times 20^{-9}$g Fe.

SUMMARY

A simple apparatus is described for the photographic measurement of the color intensity of solutions, in which a cell with a capacity of 0.05 - 0.1 ml is used.

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COPRECIPITATION OF CESIUM WITH SPARINGLY SOLUBLE DIPICRYLAMINES

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Dipicrylamine (hexanitrodiphenylamine) was first suggested by Poluetkov in 1933 [1] as a sensitive reagent for potassium. Since that time the soluble sodium and magnesium salts of dipicrylamine have found fairly wide application both for the qualitative detection of potassium, rubidium, and cesium, and for the quantitative determination of these elements [2-6].

Despite the fact that quantitative determinations of the alkali metals indicated, by means of dipicrylamine are carried out fairly often the possible coprecipitation of ions with precipitates of the dipicrylamine salts has not yet been studied. We were unable to find any published references to the coprecipitation of cesium with the sparingly soluble dipicrylamines of potassium, rubidium, thallium, and ammonium.

Meanwhile, taking into account their chemical similarity, the fact that their valencies are the same, and that the ionic radii of cesium, potassium, and thallium are similar to each other, one might expect that cesium would be coprecipitated with the dipicrylamines of these elements.

We studied the coprecipitation of cesium with the dipicrylamines, using the radioactive isotope Cs^{134} as an indicator. The initial specific activity of the preparation amounted to 130-170 impulses/minute per γ of cesium. The precipitant used was a 1% solution of sodium dipicrylamine.

Precipitation was carried out as follows. Into a series of centrifuge tubes were introduced 1-ml lots of solution containing 1 mg of potassium or 2.5 mg of thallium, as well as 12 γ of cesium; precipitation was effected by addition of 1-3 ml of sodium dipicrylamine. After one hour, the tubes were centrifuged and the cesium content of the mother liquors determined radiometrically. The mother liquors were then removed, and the precipitates transferred to filters, which were first washed with ether and then with iced water, and finally dried to constant weight.

In order to exclude the effect of the appreciable solubility of the precipitate, we determined not only the absolute amount of coprecipitated cesium, but also the amount of it in 1 mg of the precipitate.

Preliminary tests showed that cesium is almost completely coprecipitated with the dipicrylamines of potassium, rubidium, and thallium.

In order to make effective use of the coprecipitation of cesium for the purposes of concentrating the latter, we studied the nature of this process.

First of all we investigated the effect of temperature on the coprecipitation of cesium with potassium and thallium dipicrylamines. For this purpose, the working solutions were thermostated at various temperatures prior to mixing (Table 1).

As the results given in Table 1 show, on increasing the temperature from 0 to 30°, coprecipitation of cesium with potassium dipicrylamine remains almost complete. On increasing the temperature further, the amount of cesium coprecipitated decreases as the result of the increasing solubility of the precipitate but the cesium content per unit weight of the precipitate of potassium (or thallium) dipicrylamine remains constant at the

TABLE 1

Coprecipitation of Cesium with Potassium and Thallium Dipicrylamines as a Function of Temperature (12 γ cesium, 1 mg potassium, or 2.5 mg thallium)

Macro-component	Temp.	Cs coprecipitated		Wt. of prec.	Cs, in γ/mg prec.
		in γ	in %		
Potassium	0	11.7	97	9.3	1.3
	15	11.7	97	9.3	1.3
	30	11.4	95	7.9	1.4
	40	10.0	83	7.2	1.4
	80*	—	—	—	—
Thallium	0	11.8	98	9.0	1.3
	15	11.8	98	8.4	1.4
	30	11.7	97	9.0	1.3
	40	11.9	99	8.5	1.4
	80	11.7	97	8.0	1.5

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*At this temperature the residue of potassium dipicrylamine dissolves completely.

various temperatures. This signifies that temperature changes have no effect on the coprecipitation of cesium with the dipicrylamines.

We next studied the adsorption of cesium on aged precipitates of potassium and thallium dipicrylamines, prepared from 1 mg potassium or 2.5 mg thallium (Table 2).

Were the coprecipitation of cesium mainly the result of adsorption processes, then one might expect that as in the previous experiments, there would be almost complete transfer of cesium from solution to precipitate. Accordingly, on aging the precipitate for 48 hours, there should be a considerable decrease in coprecipitation. This however was not observed; this fact, coupled with the results shown in Table 1 and 2, testify to the isomorphous character of the coprecipitation of cesium with potassium and thallium dipicrylamines.

The results given in Table 3 show that the third component does not affect coprecipitation of cesium; the extent of adsorption coprecipitation also depends on the order in which the reagents are added to each other. We investigated the influence of this factor on coprecipitation of cesium. It was found that the order in which the solutions are added has no effect on the amount of coprecipitated cesium. Cesium, here again, is almost completely coprecipitated with potassium and thallium dipicrylamines.

TABLE 2

Adsorption of Cesium on Aged Precipitates of Potassium and Thallium Dipicrylamines (12 γ cesium)

Precipitate	Cesium adsorbed	
	in γ	in %
Freshly prepared potassium dipicrylamine	2.5	21
Potassium dipicrylamine allowed to stand for 48 hours	2.6	22
Freshly prepared thallium dipicrylamine	1.3	11
Thallium dipicrylamine allowed to stand for 48 hours	0.8	7

From Fig. 1 it is evident that with increasing amounts of the macro-components (thallium and potassium), or decreasing amounts of the micro-component, the amount of cesium in 1 mg of precipitate always decreases. Consequently, the amount of coprecipitated cesium in the precipitate depends, not so much on its absolute amount, but on the proportions of cesium and potassium, and also of cesium and thallium in the solution prior to precipitation.

Cesium is almost completely coprecipitated with the precipitates of potassium and thallium dipicrylamines in all cases.

Thus, variations in the conditions used for carrying out the tests have no effect on the coprecipitation of cesium with the dipicrylamines. We accordingly again came to the conclusion that this coprecipitation is isomorphous in character.

TABLE 3

Coprecipitation of Cesium (12 γ) in the Presence of a Third Component

Macro-component	Macro-component content mg/ml	Third component	Cs coprecipitated		Wt. of prec.	Cs, γ / mg prec.
			in γ	in %		
Potassium	1.0	None	11.5	95	10.4	1.1
	1.0	Rubidium	11.0	91	10.0	1.1
	1.0	Thallium	11.0	91	9.9	1.1
	1.0	Magnesium	12.0	100	10.7	1.1
Thallium	2.5	None	11.4	95	7.2	1.8
	2.5	Rubidium	11.6	96	6.5	1.8
	2.5	Thallium	11.5	95	6.2	1.9
	2.5	Magnesium	11.7	97	7.0	1.7

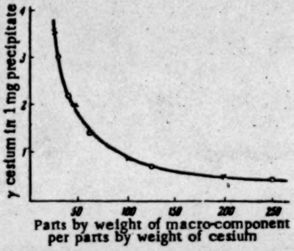

Fig. 1. Coprecipitation of cesium as a function of changes in the amounts of the macro- and micro-components. x) Experiments carried out with a constant amount of cesium; o) Experiments carried out with a constant amount of potassium or thallium.

In order to study the effect of the amount of precipitant on the coprecipitation of cesium with potassium dipicrylamine, we carried out experiments on the precipitation of the same amount of potassium (1.0 mg):

a) with the stoichiometric amount of sodium dipicrylamine;

b) with an amount of sodium dipicrylamine twice the stoichiometric amount;

c) with amounts of sodium dipicrylamine one half and one quarter the stoichiometric amounts.

About 12 mg of sodium dipicrylamine is the theoretical amount required for precipitation of 1 mg of potassium.

The experimental results (Table 4) show that with decreasing amount of precipitant the amount of coprecipitated cesium decreases, but the amount of coprecipitated cesium increases per unit weight of the precipitate as the weight of the latter decreases. This can be explained by the fact that the Khlopin constant in this case is greater than unity. Similar experiments were carried out with rubidium, thallium, and ammonium dipicrylamines (Tables 5-7).

The results given in Tables 4-7 are illustrated graphically in Fig. 2. The amount of the precipitated macro-component calculated as a percentage, from the weight of precipitate obtained, is plotted along the abscissa. We see that, other conditions being equal, most cesium is coprecipitated with ammonium dipicrylamine. The hypothesis can be advanced that the Khlopin constant is of greater importance during the coprecipitation of cesium with ammonium dipicrylamine, and of lesser importance with the corresponding salts of potassium and thallium, while in the case of rubidium dipicrylamine, Khlopin's constant approximates to unity. We did not calculate this constant, since, for the comparatively short time interval necessary for carrying out separate tests, the system only approximates to a thermodynamic equilibrium between the amount of cesium and the macro-component in the solution and precipitate.

The almost complete coprecipitation of cesium with the dipicrylamine precipitates enables one to develop a method for its concentration. Precipitation of 10 mg of the macro-component (potassium, thallium) and 12 γ of cesium contained in 100 ml of solution, was effected by addition of 200 mg of sodium dipicrylamine. The cesium content of the precipitate separated from the mother liquor after standing for 24 hours was

TABLE 4

Coprecipitation of Cesium with Potassium Dipicrylamine as a Function of the Amount of Precipitant for a Constant Amount of Potassium (1 mg potassium and 12 γ cesium)

Moles precipitant per mole K	Cs coprecipitated		Wt. of prec., mg	K prec., %	Cs, γ/mg prec.
	in γ	in %			
2	11.7	97	10.7	88	1.1
1	11.4	95	10.4	85	1.1
0.5	9.9	83	5.1	42	2.2
0.25	6.5	54	2.3	20	2.3

TABLE 5

Coprecipitation of Cesium with Rubidium Dipicrylamine as a Function of the Amount of Precipitant (2.5 mg thallium, and 12 γ cesium)

Moles precipitant per mole K	Cs coprecipitated		Wt. of prec., mg	Rb prec., %	Cs, γ/mg prec.
	in γ	in %			
1	11.3	94	14.0	91	0.8
0.5	5.0	42	7.5	49	0.7
0.25	2.6	24	3.0	19.5	0.8
0.125	1.6	13	2.5	16.2	0.7

measured radiometrically. It was found that under these conditions about 75% of the cesium was concentrated in the precipitate. By carrying out a threefold precipitation it is possible to concentrate practically all the cesium found in the original solution.

On decreasing the amount of cesium in 100 ml of solution to 0.01 γ (specific activity, 70,000 impulses/minute per γ of cesium), about 85% of the cesium is concentrated in the precipitate.

TABLE 6

Coprecipitation of Cesium with Thallium Dipicrylamine as a Function of the Amount of Precipitant (2.5 mg thallium, and 12 γ cesium)

Moles precipitant per mole K	Cs coprecipitated		Wt. of prec., mg	Tl prec., %	Cs, γ/mg prec.
	in γ	in %			
2	11.4	94	4.7	60	2.4
1	11.5	95	5.0	63	2.3
0.5	6.5	55	3.0	38	2.2

TABLE 7

Coprecipitation of Cesium with Ammonium Dipicrylamine as a Function of the Amount of Precipitant (1 mg ammonium, and 12 γ cesium)

Moles precipitant per mole K	Cs coprecipitated		Wt. of prec., mg	Ammonium prec., %	Cs, γ/mg prec.
	in γ	in %			
1.5	11.9	99	9.1	36	1.3
1	11.8	98	6.3	25	1.9
0.5	11.9	99	4.0	16	2.9

It is best to carry out separation of traces of cesium by means of ammonium dipicrylamine, which is readily broken down and removed. 100 ml of solution containing 70 mg of ammonium nitrate and 12 γ cesium

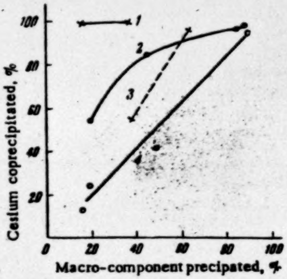

Fig. 2. Coprecipitation of cesium as a function of the amount of coprecipitated macro-component: 1) precipitation of ammonium dipicrylamine; 2) precipitation of potassium dipicrylamine; 3) precipitation of thallium dipicrylamine; 4) precipitation of rubidium dipicrylamine.

was precipitated with a solution of sodium dipicrylamine. After 24 hours the precipitate was removed from the mother liquor, transferred to a crucible and heated to 300°. Under these conditions the ammonia volatilized, the dipicrylamine decomposed, and the cesium formed the oxide. The traces of oxide thus obtained were dissolved in a drop of water. In this solution cesium was detected by formation of characteristic crystals of $Cs[BiI_4]$.

In this way, sparingly soluble dipicrylamines, particularly ammonium dipicrylamine, can be used as carriers for isolating traces of cesium from very dilute solutions.

SUMMARY

It has been established that cesium can be isomorphously coprecipitated with the sparingly soluble dipicrylamines of the alkali metals and thallium. It has been shown that thallium and ammonium dipicrylamines can be used as carriers for removing traces of cesium from very dilute solutions.

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SPECTROGRAPHIC DETERMINATION OF CALCIUM, MAGNESIUM, ALUMINUM, SILICON, AND TIN IN REFINED RHODIUM AND IRIDIUM

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During the analysis of noble metals it is often necessary to determine calcium, magnesium, aluminum, silicon, and sometimes tin which are present in small amounts difficult to evaluate by normal chemical methods. Determination of the metals indicated as impurities in refined metals should be possible by means of spectrographic analysis. During the analysis of rhodium and iridium for these elements, the metal was brought into solution and the latter evaporated in an ac arc. The success of the analysis was found to depend to a considerable extent on the use of accurately prepared standards. During the development of a technique for analyzing rhodium for its content of the elements indicated above, the starting material for preparing standards was a very pure preparation of rhodium trichlorotriamine. Nevertheless, even this preparation contained calcium, which, despite careful and repeated precipitation of the trichlorotriamine, still showed up on the spectrograms. This small amount of calcium, which possibly came from dust in the air, was taken into account in our calculations, by extrapolation. The reprecipitated rhodium trichlorotriamine was decomposed by heating in a crucible oven and was reduced in a hydrogen stream. The rhodium metal was dissolved by the aid of chlorination [1].

A few grams (3-4) of the metallic rhodium was carefully ground in an agate mortar to a very fine powder. The powder was strewn into a quartz, round-bottom flask sealed with a ground glass stopper with two outlet tubes for gas. The flask was placed in a crucible oven which could be heated to 800-900°. When the temperature in the oven had reached 200°, chlorine was passed from a cylinder into the flask, the chlorine having been washed beforehand with water in a wash bottle. Chlorine was passed through the apparatus for an hour at the rate of 2-3 bubbles per second. In the course of this time, the temperature was gradually taken up to 700°. Heating was discontinued at the end of the hour, the flask removed from the oven and cooled in air; its contents – rhodium chloride – was transferred to an agate mortar, to which was then added sodium chloride equal to twice the amount of the rhodium chloride, and the whole thoroughly ground up and mixed. The ground mixture was then replaced in the original quartz flask. The flask was placed in the crucible oven, and chlorine passed through again at the same rate as before. The temperature was raised to 700-800° and kept at that temperature for 20-25 minutes. The whole chlorination process took about an hour. At the end of this period the oven was switched off and the flask left in the oven until the latter had cooled completely, otherwise the flask might have cracked because of the rapid crystallization of the fused salts.

The contents of the cooled flask were dissolved in 90 ml of twice-distilled water. The insoluble residue was filtered off. The volume of the solution was made up to 100 ml. 5 ml of this solution was taken and its rhodium content determined chemically. This solution of sodium chlororhodiate plus some sodium chloride was taken as the stock solution for preparing the standard solutions.

The impurities to be determined were taken in the form of solutions of the following salts: calcium sulfate, the double sulfate of magnesium and aluminum, aluminum nitrate, sodium silicate, and tin chloride. Sodium silicate was prepared by fusing chemically pure silica with sodium carbonate, the melt formed being dissolved in water and the silicon content determined chemically.

Using these solutions of sodium chlororhodiate and the salts of calcium, aluminum, silicon, and tin, standard solutions were prepared by mixing; the standard solutions prepared contained the impurities to be determined in amounts aranging from 0.065 to 0.0003% with respect to rhodium. The rhodium concentration was 0.5%.

The standard solutions prepared in this way were placed in a discharge tube with carbon electrodes. The gap between the carbon electrodes was kept at 3 mm.

An ac arc was used for excitation.

The current used had a value of 3 amperes. The exposure time for calcium and magnesium was 3 minutes, while for silicon, aluminum, and tin at low concentrations, it was 5 minutes. Solution was added to the discharge tube every 1.5 minutes during the exposure. Each standard solution was exposed three times.

The electrodes were arced for 10-15 minutes prior to each exposure. The spectra were photographed on NIKFI spectrographic plates type II. The plates were developed in a metol-hydroquinone developer. Photometric measurements were carried out with a Zeiss microphotometer.

Determination of Calcium. The following pairs of lines were chosen for the spectrographic determination of calcium:

Ca I 4226.728 A – Rh I 4196.504 A
Ca II 3968.468 A – Rh II 3975.314 A

The calibration curves for each pair of lines (Fig. 1 a, b) covered the concentration range of calcium in rhodium from 0.06 to 0.002%. Both pairs of lines gave steep curves with a slope for the first pair of 44° ($\tan \alpha = 0.966$), while for the second the slope was 49° ($\tan \alpha = 1.150$).

The amount of calcium in the original rhodium was determined graphically; i.e. the spectrum of the solution of pure rhodium was also photographed; the results of the photometric measurements were superimposed on the curve and the calcium content found by extrapolation. On the basis of the calcium content found, corrections were applied to its concentration in the standard solutions.

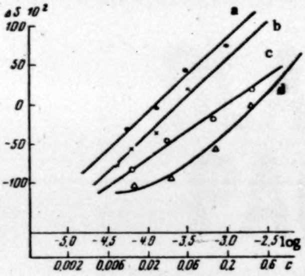

Fig. 1

The spectra of the solutions were photographed on several plates. On plates of the same type, the tangent of the slope of the curve varied little around the values given above.

The mean arithmetical error for determination of calcium by means of the first pair of lines, on the basis of several negatives, amounted to 11% for the concentration range 0.065-0.005. For the second pair this error was 9%.

During analysis for calcium the lower concentration limit was set by the content of the element to be determined in the rhodium. If rhodium of higher purity with respect to calcium were available, the concentration of the latter which could be determined could be lowered by one order.

Determination of Magnesium in Rhodium. The standard solutions used contained 0.0035, 0.0065, 0.0235, and 0.0635% magnesium with respect to rhodium.

The following pairs of lines were chosen for analysis:

Mg I 2852.129 A – Rh I 2862.935 A
Mg I 2852.129 A – Rh II 2845.753 A

The tangent of the slope of the curve for the first pair of lines was 0.781 (angle 38°), while for the second pair of lines it was 0.869 (41°). The mean deviation for the first pair of lines on the basis of several negatives was 7%, while for the second it was 13%; consequently, the first pair of lines are to be recommended (Fig. 2 a).

Determination of Aluminum. There was no aluminum present in the test rhodium. The pair of lines Al I 3092.713 A and Rh I 3087.415 A were chosen for photometric measurements, and also the same line for aluminum with respect to the immediate background. Since the pairs of lines Al–Rh, and Al – background both gave flat curves, errors for determination of aluminum were considerable, amounting to 20%. The curve obtained for these lines is shown in Fig. 2b.

Determination of Silicon and Tin. The calibration curve for the determination of silicon was constructed on the basis of photometric results for the following pairs of lines for silicon - rhodium:

Si I 2881.578 A – SiI – 2516.123 A
Rh 2882.366 A – RhI – 2515.746 A

(Fig. 1 c, d), for the first pair of lines the tangent of the slope was 0.649, while for the second it was 0.900.

The original rhodium contained no silicon.

The sensitivity of tin determination for contents of the latter in solution below 0.0001% was low, and the lines had low intensity; accordingly, for the determination of this element, it is necessary to have more concentrated solutions with the same ratio of tin to rhodium. Only one pair of lines were measured photometrically: Sn I 3034.121 A – Rh I 3023.911 A.

The other analytical lines of tin proved to have low sensitivity.

The deviation from the calibration curve of points corresponding to equal concentrations, as determined by the photometric results (Fig. 2 c) amounted to 17%.

In developing a method for the spectrographic analysis of refined iridium for its content of calcium, magnesium, silicon, aluminum, and tin, the first difficulty that cropped up was the absence of iridium which was spectrographically pure with respect to the impurities listed above, and the absence of a method of purifying iridium from small amounts of calcium, magnesium, and aluminum.

The iridium which we had at our disposal contained perceptible amounts of calcium and magnesium, and consequently could not serve as original material for preparing standards. It was necessary to free it from these impurities.

As in the case of rhodium, iridium was brought into solution by chlorination. An aliquot of the metal which was chlorinated with sodium chloride was almost quantitatively converted into sodium chloroiridiate.

The solution which was prepared in the same way as rhodium was spectrographically analyzed for Ca, Mg, Al, Si, and Sn. The solution of the iridium salt was found to contain calcium, so that this solution as such could not be used for preparing standards, and had to be freed from calcium.

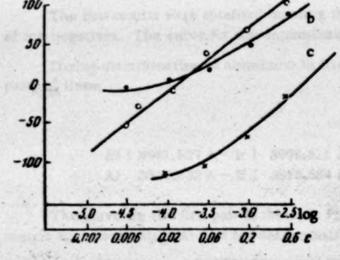

Fig. 2.

The sodium chloroiridiate obtained by chlorination was recrystallized twice, but its calcium content did not drop; accordingly, coprecipitation of calcium with lanthanum oxalate was tried.

Crystalline oxalic acid (2-3 g of acid per 3-4 g of metal) was added to the solution of sodium chloroiridiate; concentrated lanthanum nitrate was then added with stirring until the oxalic acid had been completely precipitated. The lanthanum oxalate formed should trap the calcium oxalate. The precipitate was filtered off, and some more crystalline oxalic acid added to the filtrate of sodium chloroiridiate; lanthanum nitrate was again added. This procedure was repeated three times so that all the lanthanum was precipitated.

As a result of this procedure, the calcium content of the chloroiridiate decreased appreciably. The sodium chloroiridiate purified in this way was analyzed chemically for its iridium content; for this purpose 5 ml of the solution was carefully evaporated to dryness in a tared quartz crucible on a water bath. The crucible and its contents were then calcined in a crucible oven for complete decomposition of sodium chloroiridiate. The decomposition product was carefully washed free from sodium chloride by means of hot water, and calcined in a stream of hydrogen. The reduced metal was then weighed.

From the solution of chloroiridiate whose iridium content had been determined as described above, a solution was prepared which contained 1% of iridium. The elements which were to be determined as impurities in the iridium were used in the form of the same salts as those used for the preparation of rhodium standards. The original solutions of the salts contained 0.02% each of Ca, Mg. Al, and Sn and 0.01% Si.

From these solutions, standard mixtures were prepared containing 0.5% and 3×10^{-4}% of Ca, Mg, Al, Si, and Sn taken separately; this corresponded to 0.06-0.0006% of these elements with respect to iridium.

The lower limit for the determination of calcium proved to be its content in iridium as determined by extrapolation.

Excitation conditions, conditions for taking photographs of the spectra, loading the discharge tube, etc. were similar to those used in the case of rhodium.

The following pairs of lines were chosen for determination of calcium:

	tan α	Mean deviation, in %
Ca I 4226.728 A – Ir 4210.587 A	1.111	7
Ca II 3968.468 A – IrI 3976.311 A	1.327	6
Ca II 3933.666 A – Ir 3915.384 A	1.0	9

The mean deviation from the curve was determined on the basis of seven negatives for each pair of lines.

As an example we show in Fig. 3 b the curve for the pair of lines Ca 3968.478 A and Ir I 3976.311 A, which has the steepest slope.

The analytical pairs of lines used for magnesium determination were the following:

	tan α	Mean deviation, in %
Mg II 2795.530 A – Ir I 2800.820 A	1.111	6
Mg I 2852.129 A – Ir I 2849.725 A	0.839	13
Mg II 2802.695 A – Ir I 2800.820 A	0.933	11

The best results were obtained on using the first pair of lines. The deviation was calculated as the mean of ten negatives. The curve for the determination of magnesium in iridium is shown in Fig. 3a.

During determination of aluminum in iridium almost equally good results were given by the following pairs of lines:

	tan α	Mean deviation, in %
Al I 3961.527 A – Ir I 3976.311 A	0.679	12
Al 3944.032 A – Ir I 3915.384 A	0.577	14

The curve for the first pair is shown in Fig. 4a. Only one pair of lines, which was suitable for photometric measurements, was used for determination of silicon.

The pair used was Si I 2881.578 A Ir 2880.211A (Fig.4b), the curve obtained for this pair was not steep enough, and many of the silicon lines were not observed at all on the negatives. The mean deviation from the calibration curve amounted to about 20% in this case.

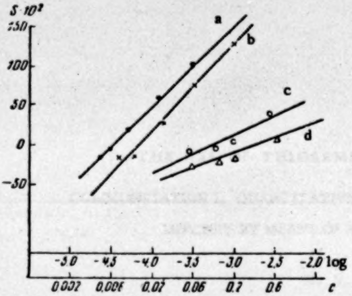

Fig. 3.

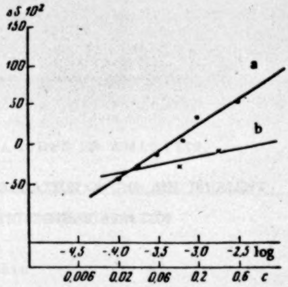

Fig. 4.

The pair of lines Sn I 3034.121 A, Ir I 3032.410A was used for tin determination. This pair gave a curve whose slope was 0.625 while the deviation from the curve amounted to 10% on the average. Another pair of lines Sn 3175.019 A, Ir 3177.582 A was also found to be suitable; in this case, however, the slope of the curve was less (Fig. 3 c, d).

It should be pointed out that the sensitivity for the determination of tin in iridium is not high, and the lower limit of the tin concentration which can be determined is 0.4% with respect to iridium.

SUMMARY

A technique has been developed for the spectrographic determination of calcium, magnesium, aluminum, silicon, and tin in refined rhodium and iridium.

A method is described for the preparation of standard solutions of rhodium and iridium containing small amounts of calcium, magnesium, aluminum, silicon, and tin.

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THE USE OF THIOSEMICARBAZIDES IN ANALYSIS

COMMUNICATION I. QUANTITATIVE DETERMINATION OF UNI- AND DIVALENT MERCURY BY MEANS OF 1-PHENYLTHIOSEMICARBAZIDE

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Of the methods for determining uni- and divalent mercury, the most widespread are those based on titration with ammonium thiocyanate or sodium chloride [1]. During determination of small amounts of divalent mercury, good results are obtained by titrating with potassium iodide [2]. Iatsimirskii and Astashev [3] have developed a method for determining mercury by means of thiourea. Kuznetsov and Mitrofanova [4] have suggested the determination of gamma amounts of mercury by means of stilboxine. Other methods have been described in the literature, but most of them are only applicable to the determination of univalent or divalent mercury, and do not permit determination of total uni- and divalent mercury. As a result of this, for example, during the determination of univalent mercury by means of a method which is really meant for determination of divalent mercury, it is necessary to oxidize the univalent mercury beforehand and this step means, in a number of instances, the introduction of complications, and limits the applicability of many methods.

The present article describes results obtained during the application of 1-phenylthiosemicarbazide as a reagent for the quantitative determination of mercury by a titrimetric method based on the reaction: $Hg(NO_3)_2 + 2C_6H_5NHNHCSNH_2 \rightarrow [Hg(S_6H_5NHNHCSNH_2)_2]^{2+} + 2NO_3^-$. As a result of the insignificant dissociation of the complex $[Hg(C_6H_5NHNHCSNH_2)_2]^{2+}$ the equilibrium of the reaction shifts almost completely to the right.

As compared with other similar methods, when 1-phenylthiosemicarbazide is used, it is possible to determine both uni- and divalent mercury. The indicator used is a 0.1 N solution of copper nitrate. During the interaction of very dilute solutions of 1-phenylthiosemicarbazide with copper nitrate, sulfate, chloride, or acetate the solution is colored an intense blue color as the result of the formation of a soluble complex:

$$Cu(NO_3)_2 + 2C_6H_5NHNHCSNH_2 \rightarrow [Cu(C_6H_5NHNHCSNH_2)_2]^{2+} + 2NO_3^-$$

With concentrated solutions of reactants, the solution acquires a dark blue color, and a precipitate may form. On addition of a solution of mercury nitrate to a solution of 1-phenylsemicarbazide and the copper complex $[Cu(C_6H_5NHNHCSNH_2)_2]^{2+}$, there occurs, in the first instance, a reaction between mercury ions and the molecules of 1-phenylthiosemicarbazide. Subsequently, there occurs substitution of copper ions in the complex $[Cu(C_6H_5NHNHCSNH_2)_2]^{2+}$ by Hg ions, with formation of a more stable complex ion $[Hg(C_6H_5NHNHCSNH_2)_2]^{2+}$. The blue color of the solution thereupon changes to yellow or weak-yellow, depending on the concentration of the solution. Thus, the equivalence point is determined by the color change from blue to yellow. During determination of of univalent mercury is is essential to bear in mind that in a solution of its salts, there exists the equilibrium $[Hg_2]^{2+} \rightleftharpoons Hg^{2+} + Hg$. 1-Phenylthiosemicarbazide, which forms a stable complex $[Hg(C_6H_5NHNHCSNH_2)_2]^{2+}$, with Hg^{2+} ions, displaces this equilibrium to the right: $[Hg_2]^{2+} + 2C_6H_5NHNHCSNH_2 \rightarrow$ $\rightarrow Hg + [Hg(C_6H_5NHNHCSNH_2)_2]^{2+}$. During this reaction fine drops of metallic mercury separate out; in order to eliminate the effect of this mercury on the determination of the equivalence point, the solution of 1-phenylsemicarbazide should be diluted with water at the rate of 75-100 ml of water per ml of an acetic acid solution of 1-phenylsemicarbazide before carrying out the titration. Under these conditions, the color change of the solution from blue to yellow can be determined fairly accurately, and the liberation of metallic mercury does not affect the accuracy of determination.

The method suggested permits small amounts of univalent and divalent mercury to be determined accurately in dilute solutions of nitrates. Chlorine and bromine ions, however, complicate determination of mercury. In the latter case, the reaction between 1-phenylthiosemicarbazide and mercuric ions is slow, and the color change from blue to yellow is not clear cut.

For the determination of mercury in chlorides or bromides it is essential to convert them first to the nitrate, for which purpose an excess of sodium hydroxide solution is added to the test solution. The precipitated mercury oxides are filtered off, washed with water, and dissolved in nitric acid; the mercury is then determined in the solution thus obtained. Most cations and anions do not interfere with the determination of mercury. Analysis can be carried out in acid media over a wide pH range. In contrast to most other analogous organic compounds, 1-phenylthiosemicarbazide forms a compound with a constant composition with mercury. 1-Phenylthiosemicarbazide which is readily synthesized from ammonium thiocyanate and phenylhydrazine hydrochloride can be recrystallized easily and prepared in a chemically pure form. Its acetic acid solution,which is used for mercury determination, can be stored for long periods without any appreciable change.

When calculating the results one should bear in mind that the gram-equivalent of 1-phenylthiosemicarbazide is equal to its molecular weight. 1 ml of a 0.05 N solution of 1-phenylthiosemicarbazide is equivalent to 5.015 mg of divalent mercury and 10.03 mg univalent mercury.

For the quantitative determination of 1-phenylthiosemicarbazide and other thiosemicarbazides, they are titrated with a solution of mercuric nitrate using copper nitrate as indicator. By using 0.1-0.05 N mercuric nitrate, it is possible to determine macro- and micro-amounts of 1-phenylthiosemicarbazide and other thiosemicarbazides. The mercuric nitrate solution is standardized against an exact aliquot of 1-phenylthiosemicarbazide.

The order in which titration is carried out is of essential importance. During the determination of both thiosemicarbazides and mercury, it is essential that the solution of mercurous or mercuric nitrate be added to the solution of the thiosemicarbazide.

1-Phenylthiosemicarbazide was prepared from phenylhydrazine hydrochloride and ammonium thiocyanate as follows. 152.24 g of ammonium thiocyanate (2 moles) and 144.5 g (1 mole) of phenylhydrazine hydrochloride were measured out into a 500-ml flask, and the mixture covered with 200 ml of acetic acid. The flask was fitted with a reflux condenser and was heated on a boiling water bath for 2 hours. The contents of the flask were periodically shaken, whereupon the ammonium thiocyanate and phenylhydrazine hydrochloride dissolved completely. Hydrogen sulfide was liberated during the reaction.

250-300 ml of water was added to the solution when heating was finished. The precipitate which separated out on cooling was filtered on a Buchner funnel, washed with water, and then recrystallized from alcohol. The yield of recrystallized product, after drying in a thermostat at 105-110° amounted to 60 g; the melting point was 197-198°. According to published data, the melting point of 1-phenylthiosemicarbazide is 200-201°. The product obtained dissolves readily in alcohol andin acetic acid but is less soluble in water and in benzene.

Synthesis of 1-phenylthiosemicarbazide can be carried out in an aqueous medium by heating the reactants to the boiling point for 2 hours. The yield of the finished product in this instance will be somewhat less. Potassium thiocyanate can be used instead of ammonium thiocyanate.

Standard solutions of 1-phenylthiosemicarbazide (0.04-0.005 N) were prepared by dissolving the exact aliquots of the chemically pure reagent in 70-80% acetic acid on heating in a standard flask. The titer of the solution does not change over a long period of time.

For analysis, the test solution of mercury salt was placed in a standard flask and the volume made up to the mark with water. For this purpose it is necessary that the concentration of the test solution should be 0.1-0.5 N.

An exact amount of the acetic acid solution of 1-phenylthiosemicarbazide was measured out from a macro- or micro-buret; to this solution 2-3 drops of a 0.1 N solution of cupric nitrate was added, after which the solution of 1-phenylthiosemicarbazide was titrated with mercuric nitrate solution until the color of the solution changed from blue to yellow or weakly yellow.

For the determination of mercurous nitrate, 1-3 ml of the acetic acid solution of 1-phenylthiosemicarbazide was measured out of a micro-buret into a conical flask, and the solution diluted with water on the basis of 75-100 ml of water to each milliliter of 1-phenylthiosemicarbazide. After addition of 0.5-1 ml of 0.1 N cupric nitrate, the contents of the flask were titrated against a standard solution of mercurous nitrate from a micro-buret until the color of the solution changed from blue to a weak grey-yellow.

TABLE 1

Determination of Mercury in $Hg_2(NO_3)_2$

$C_6H_5N_2H_2 \cdot CSNH_2$ taken in mg as a soln.	Water added, in ml	Mercury found, in mg	Mercury taken, in mg
7.0	75	8.39	8.33
7.0	100	8.39	8.35
7.0	150	8.39	8.42
14.0	125	16.77	16.80
14.0	250	16.77	16.85
14.0	200	16.77	16.85

TABLE 2

Determination of Mercury in $Hg(NO_3)_2$

$C_6H_5N_2H_2 \cdot CSNH_2$ taken in mg, as a soln.	Mercury found, in mg	Mercury taken, in mg
70.0	41.93	42.08
70.0	41.93	42.08
105.0	63.08	63.186
140.0	83.86	83.66
140.0	83.86	83.66
35.0	20.46	20.40
35.0	20.46	20.40
14.0	8.38	8.38
14.0	8.38	8.35

The color of the solution changes very sharply on addition of one drop of the test solution in excess. In order to avoid overstepping the endpoint, the solution of mercuric nitrate should be added slowly, with careful stirring of the solution, toward the endpoint.

Silver, chloride, bromide, and quadrivalent tin ions interfere with the mercury determination.

The results obtained are given in Tables 1 and 2.

SUMMARY

1. A method has been developed for the quantitative determination of uni- and divalent mercury, by titration with 1-phenylthiosemicarbazide in the presence of cupric salts as indicator.

2. A method is suggested for the quantitative determination of 1-phenylthiosemicarbazide and other thiosemicarbazides by titration with mercuric nitrate.

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* Original Russian pagination. See C.B. Translation.

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DIALKYL- AND DIARYLDITHIOPHOSPHORIC ACIDS AS ANALYTICAL REAGENTS

COMMUNICATION 4. SEPARATION OF CADMIUM FROM ZINC AND OTHER ELEMENTS. GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF CADMIUM*

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It has been pointed out before [1-2] that diethyldithiophosphoric acid $(C_2H_5O)_2PSSH$ and its soluble salts, as well as other dithiophosphates quantitatively precipitate a number of heavy metals, many of which give sparingly soluble sulfides. In general, the dithiophosphates are reminiscent in their properties of the dithiocarbamates which are widely used in analytical practice, and also of the xanthogenates, but they differ from them in exhibiting greater selectivity. Thus, the dithiophosphates do not precipitate elements of the third analytical group, including zinc. The exception is trivalent iron which, at a certain hydrochloric acid concentration, forms a black precipitate. At the same time, cadmium belongs to the number of those elements which form sparingly soluble compounds with dialkyl- and diaryldithiophosphates. This opens up the possibility of developing a method for the quantitative separation of cadmium from zinc, and also from other elements of groups I, II, and III.

Separation of cadmium from zinc is of great practical importance, since both these elements often occur together in natural and industrial products, while at the same time there is a real need for simple, rapid, and accurate methods for separating cadmium from zinc, which would satisfy the requirements of production control. Serious difficulties have been caused by the absence of selective reactions for cadmium and zinc. The close similarity between the chemical properties of cadmium and zinc seriously limit the possibilities of developing methods for their separation, and of developing methods for determination of cadmium in the presence of zinc. A review of methods for determining cadmium, and for separating it from zinc and other elements is to be found in the well-known textbook of Fresenius and Jander [4]. Most of the gravimetric [5-9], titrimetric, and other methods for determining cadmium, assume that zinc is absent. There are a number of methods at present for separating cadmium from zinc, and for the determination of cadmium in the presence of zinc. Cadmium can be separated from zinc and some other elements by precipitation with hydrogen sulfide from acid solution [4], or by precipitation with thiourea from an alkaline cyanide solution [10]; precipitation of cadmium by means of Reinecke's salt in the presence of thiourea is widely used, the cadmium is precipitated as $[Cd(CSN_2H_4)_2][Cr(SCN)_4(NH_3)_2]$ [11-14]. Precipitation of cadmium by means of 2-(o-hydroxyphenyl)-benzoxazole from an alkali solution containing tartrate permits quantitative separation of cadmium from zinc and other elements [15]. For determination of cadmium in the presence of zinc, methods have been developed which are based on the precipitation of the complex anions $[CdI_4]^{2-}$ or $[CdBr_4]^{2-}$ by organic bases. The precipitates obtained are weighed. Titrimetric or photometric finishes for the determination of cadmium are much rarer. β-Naphthoquinoline [16-18], methyl violet [19], brucine [20], and other materials have been used as precipitants for the anion $[CdI_4]^{2-}$, while brucine [21, 22], antipyrine [23, 24], diantipyrylmethane [25], and diantipyrylorthohydroxyphenylmethane [26] have been used for precipitating $[CdBr_4]^{2-}$. There are methods for separating cadmium and zinc based on ion exchange [27-29], and by means of activated metallic copper [30]; in the latter method, the metallic copper removes cadmium from a cyanide solution containing tartrate, while all the zinc remains in solution. Cadmium can be very conveniently determined in the presence of zinc by a polarographic method [31-43]. This method is very often used for production control. Relatively reliable results are obtained during the separation of zinc and cadmium, and during their determination in each others presence by the method of internal electrolysis [44-45], by fractional titration with amalgam [46], by deposition of cadmium on an aluminum cathode [47], or by electrolysis with a mercury electrode [48]. Of other methods for separating cadmium and zinc, and for determining cadmium in the presence of zinc, mention may be made of the potentiometric ferrocyanide method [49], and the potentiometric xanthogenate method [50].

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* For Communication 3, see [3].

During precipitation of cadmium with hydrogen sulfide or thiourea, coprecipitation of zinc occurs; in order to get more reliable results, precipitation has to be repeated. The Reineckate method has some essential advantages over the sulfide and some other methods; accordingly, it has received fairly wide application in practice during production control, although it is not free from drawbacks. Songina [14] has shown that the composition of the precipitate obtained in practice does not accurately correspond to the formula $[Cd(CSN_2H_4)_2][Cr(SCN)_4(NH_3)_2]_2$. Thus, in order to calculate the amount of cadmium, an empirical factor is employed which has to be determined for each batch of Reinecke's salt. The other chemical methods have not been widely used, mainly because of the fact that the reagents are not readily available or because of the rather complex procedures involved.

The search for new methods of separating cadmium from zinc, and for methods of determining cadmium quantitatively in the presence of zinc is of undoubted practical interest.

EXPERIMENTAL

Reagents and Apparatus

1. Standard solutions of cadmium sulfate were prepared by dissolving the exact amounts of analytical grade material. The solutions were standardized by precipitating the cadmium with anthranilic acid and weighing the precipitate obtained [4].

2. The 0.05 solution of nickel diethyldithiophosphate used as precipitant $[(C_2H_5O_2)PSS]_2Ni$ was prepared by dissolving the purified preparation in water. The synthesis and purification of nickel diethyldithiophosphate have been described earlier [1]. Other nickel dialkyl- and diaryldithiophosphates have been synthesized by similar methods [3]. Potassium diethyldithiophosphate was also used in the course of the work.

3. Standard iodine and sodium thiosulfate solutions were prepared by the usual methods. The sulfates, nitrates, and chlorides of group I, II, and III metals, used in the course of the work, were either analytical grade or pure grade materials, and were used without additional purification.

The Properties of Cadmium Dialkyl- and Diaryldithiophosphates

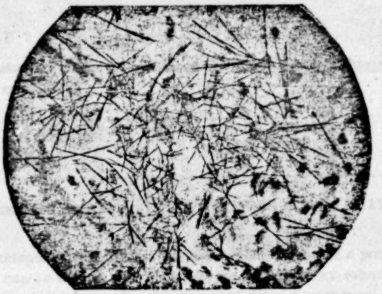
Cadmium dialkyl- and diaryldithiophosphates separate out as white, flocculent, crystalline precipitates on addition of the appropriate dialkyl- or diaryldithiophosphate in the form of the nickel or potassium salt to a solution of cadmium sulfate. Changes in the concentration of sulfuric and nitric acids over a wide range (from 0 to 6 moles/liter) have almost no effect on precipitation of cadmium. The reason is that the dialkyl- and diaryldithiophosphoric acids are strong acids; titration curves for solutions of diethyldithiophosphoric acid and sulfuric acid with KOH of the same molarity are almost identical to one another, both with respect to shape, and the value of the jump at the equivalence point. At high concentrations of nitric acid in the solution from which precipitation is to be effected, oxidation of the anion of the dithiophosphoric acid to the disulfide occurs. At mineral acid concentrations in excess of 6 moles/liter, signs can be observed of the decomposition of the dithiophosphoric acid.

The cadmium precipitates formed are almost insoluble in solutions of strong mineral acids, but readily dissolve in organic solvents which are immiscible with water (in the presence of dilute acids) to form colorless solutions; they also dissolve in ammonia.

Under the microscope (magnification 80) cadmium diethyldithiophosphate shows up in the form of characteristic needle-shaped crystals (Fig.) which permit cadmium to be detected microcrystalloscopically in the presence of ions of Group I, II, and III and also of some Group IV ions. When excess reagent is used, cadmium can be detected in the presence of 100 times its amount of copper, lead, and bismuth, at a dilution (relative to cadmium) of 1 : 50,000. The limiting dilution when the test is carried out in a test-tube is 1 : 150,000.

Cadmium diethyldithiophosphate melts at 144°.

Cadmium diethyldithiophosphate, after washing with water and drying in air to constant weight, was analyzed by the method described previously [2]. Results of numerous determinations of cadmium in the form of its anthranilate, of sulfur as barium sulfate, and of phosphorus as magnesium pyrophosphate – these results have been left out for the sake of brevity – as well as results of the iodometric titration of the precipitate (Table 1), and the result of numerous determinations of cadmium by weighing as the diethyldithiophosphate (some of these results are given below), demonstrate convincingly that the composition of the precipitate corresponds to the formula $[(C_2H_5O)_2PSS]_2Cd$.



Crystals of cadmium diethyldithiophosphate precipitate.

The approximate solubility of cadmium diethyldithiophosphate in water was determined by evaporating a known volume of the saturated solution and weighing the residue. The saturated solution was prepared by periodically shaking 1-2 g of the freshly prepared, thoroughly washed preparation with 4 liters of distilled water at room temperature (18-20°). The solution obtained was filtered, and 1 or 2 liters of the filtrate evaporated in a large beaker on a water bath of a volume of 4-5 ml, the beaker being shielded so that no dust got in. On evaporation to this volume, large, well-formed, needle-shaped crystals of cadmium diethyldithiophosphate separated out; these were filtered through a porcelain micro-crucible dried beforehand at 105°. The saturated aqueous solution of cadmium diethyldithiophosphate was used for transferring the crystals quantitatively to the crucible. The crucible plus precipitate were dried at 105° to constant weight. The melting point was then determined in order to make sure that no decomposition of the material had occurred during the process of prolonged evaporation. In all cases the melting point was 144°; thus cadium diethyldithiophosphate does not undergo any appreciable decomposition under the experimental conditions used.

Table 2 contains the results obtained.

Saturation is only attained after 20-25 days. Saturation is reached more rapidly by shaking more often. The solubility of cadmium diethyldithiophosphate can be regarded as being equal to 0.118 g in 1 liter of water at 18-20°, or 2.4×10^{-4}

TABLE 1

Iodometric Titration of Cadmium Diethyldithiophosphate*

Sample wt, in g	Found, in g	Error	
		Absolute, in g	Relative, in %
0.1649	0.1657	0.0008	+0.5
0.2020	0.2026	0.0006	+0.3
0.2344	0.2340	0.0004	−0.4

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* The precipitate was dissolved in concentrated hydrochloric acid and 2-3 ml of CCl_4 added, this was followed by an equal volume of water and an excess of a standard iodine solution; the solution was then slowly titrated with sodium thiosulfate. For the reaction between iodine and diethyldithiophosphate see [1]. The amount of precipitate was calculated on the basis of the formula $[(C_2H_5O)_2PSS]_2Cd$.

mole/liter. The solubility product:

$$L_S\,[(C_2H_5O)_2PSS]^- \cdot [Cd^{2+}] = 5.8 \cdot 10^{-11}.$$

A similar value for the solubility of cadmium diethyldithiophosphate in water was found by V. M. Byrko [51] using a radiometric method.* The solubility of cadmium diethyldithiophosphate drops sharply in the presence of excess precipitant, but it is still high enough to lead to low results during the gravimetric determination of cadmium.

TABLE 2

Determination of the Solubility of Cadmium Diethyldithiophosphate in Water at 18-20°

Period of saturation, in days	8	10	30	60	90
Concentration, in g/liter	0.0303	0.0640	0.117	0.117	0.121

Cadmium diethyldithiophosphate satisfies the basic requirements of a precipitate suitable for gravimetric determination. Cadmium can be almost quantitatively precipitated from solution as the diethyldithiophosphate when it is precipitated from relatively small volumes by means of excess precipitant. In this way the error resulting from the solubility of the precipitate drops from 0.1-0.2 mg (the limit of the sensitivity of the analytical balance). It is necessary to wash the precipitate with a saturated aqueous solution of cadmium diethyldithiophosphate, and not with distilled water or a 1% solution of ammonium nitrate. When a precipitate is washed with portions of water during determination of 0.0020-0.04 g of cadmium, the results were always low by 3-5%. Precipitation of cadmium with diethyldithiophosphate is fairly specific. A very important fact is that zinc is not precipitated even when present in appreciable concentrations. Divalent iron, aluminum, gallium, nickel, cobalt, chromium, manganese, the alkaline-earth elements, and the alkali metals also remain in solution. Other ions (at any concentration) do not prevent formation of the precipitate of cadmium diethyldithiophosphate. After washing, the precipitate is almost free of foreign ions; thus coprecipitation is expressed only to a very weak degree. The precipitate is readily filtered and washed. Cadmium, in addition to being separated quantitatively, can be weighed as its diethyldithiocarbamate, since this compound after drying at room temperature, or at 105°, has a strictly defined composition corresponding to the formula $[(C_2H_5O)_2PSS]_2Cd$ (the conversion factor to cadmium is 0.2328). The cadmium compound is completely stable to washing and drying, it is not appreciably hygroscopic, and does not lose weight during drying.

For the gravimetric determination of cadmium, 0.05 M nickel or potassium diethyldithiophosphate solution in an excess of one and a half or twice the amount of cadmium, is added to 10-100 ml of a nitric or sulfuric acid solution containing 0.002-0.1 g of cadmium, as well as zinc and other metals (in the form of chlorides for example); the precipitate formed is allowed to stand in the solution for several minutes, after which it is filtered off through a tared No. 3 sintered glass filter; the precipitate is then washed with small portions of a saturated aqueous solution of cadmium diethyldithiophosphate until the washings give a negative reaction for nickel with dimethylglyoxime (after addition of ammonia); the precipitate is finally dried to constant weight at 105°. Results of such determinations are given in Table 3.

For the accurate determination of small amounts of cadmium, a titrimetric method, based on the oxidation of the organic component of the precipitate of cadmium diethyldithiophosphate by means of iodine in a strongly alkaline medium, is very convenient.

The precipitate of cadmium diethyldithiophosphate which has been filtered through a No. 3 glass crucible and washed with small portions of water 3-4 times, is treated on the filter with 6 N sodium hydroxide in order to break down the diethyldithiophosphate, and to create a strongly alkaline medium. The amount of alkali taken is such that after addition of iodine solution, the alkali concentration in the final solution is

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* For results on the determination of the solubility of cadmium diethyldithiophosphate in the presence of ions of diethyldithiophosphoric acid at various ionic strengths, see [5].

TABLE 3

Determination of Cadmium by Precipitating and Weighing as $[(C_2H_5O)_2PSS]_2Cd$

Taken, in g		Found, in g		Error	
Cd	salt	CdR_2	Cd	Absolute, in g	Relative, in %
0.0431	1.5 $ZnSO_4 \cdot 7H_2O$	0.1847	0.0429	−0.0002	−0.4
0.4331	1.5 $ZnSO_4 \cdot 7H_2O$	0.1850	0.0430	−0.0001	−0.2
0.0431	1.5 $MgSO_4$	0.1847	0.0430	−0.0001	−0.2
0.0431	1.5 $MgSO_4$	0.1852	0.0431	0	0
0.0431	1.5 $Cr_2(SO_4)_3$	0.1835	0.0427	−0.0004	−0.9
0.0258	2 $Al(NO_3)_3$	0.1107	0.0257	−0.0001	−0.2
0.0258	1.5 $Fe_2(SO_4)_3$	0.1102	0.0256	−0.0002	−0.4
0.0258	2 $CoSO_4$	0.1101	0.0256	−0.0002	−0.4
0.0258	1.5 $Ni(NO_3)_2$	0.1104	0.0256	−0.0002	−0.4
0.0431	1.5 Na_2SO_4	0.1847	0.0429	−0.0002	−0.4
0.0431	1.5 KNO_3	0.1845	0.0429	−0.0002	−0.4
0.0431	1.5 NH_4NO_3	0.1853	0.0430	−0.0001	−0.2
0.0258	2 KCl	0.1103	0.0256	−0.0002	−0.4

0.5-1.5 N. Excess standard iodine solution is added; after 5-10 minutes the solution is acidified with sulfuric acid until the solution gives a weakly acid reaction with universal indicator paper; excess iodine is titrated with thiosulfate. Calculations are based on the equation:

$$[(C_2H_5O)_2PSS]_2Cd + 16I_2 + 42NaOH = 2(C_2H_5O)_2POONa + 4Na_2SO_4 + 32NaI + Cd(OH)_2 + 20H_2O$$

The method described for the separation of cadmium from zinc and other elements, and for the gravimetric determination of cadmium gives completely satisfactory results. Changes in hydrochloric acid concentration over a wide range do not have appreciable effects on the results of cadmium determination. The method of drying the precipitate of cadmium diethyldithiophosphate (drying to constant weight in air at 105°, and over sulfuric acid) has little effect on the experimental results. Appreciable amounts of zinc, nickel, cobalt, aluminum, chromium, iron, magnesium, beryllium, the alkaline-earths, and the alkali metals do not interfere with cadmium determination. Heavy metals which are precipitated by diethyldithiophosphoric acid in an acid medium interfere.

TABLE 4

Determination of Cadmium by Oxidation of the Organic Component of the Diethyldithiophosphate Precipitate by Iodine in a Strongly Alkaline Medium

Cadmium taken, in mg	Cadmium found, in mg	Error	
		in mg	in %
11.24	11.21	−0.90	0.3
5.62	5.65	−0.03	0.5
0.562	0.562	0	0
0.562	0.550	−0.012	2

On the basis of the method described for the separation of cadmium from zinc and other elements, and of the methods for the gravimetric and titrimetric determination of cadmium, it is easy to develop simple, rapid, and accurate analytical methods which would be applicable to various natural and industrial materials, and for production control [52]. Potentiometric titration of cadmium with a solution of nickel diethyldithiophosphate by means of a platinum electrode covered with mercury, is accompanied by a hardly perceptible potential jump at the equivalence point, accordingly, such a method is of no practical importance. Amperometric titration in a supporting electrolyte of various salts (with a mercury electrode, and on the basis of the current obtained by the reduction of cadmium) did not give satisfactory results either.

Direct photometric determination of cadmium as its diethyldithiophosphate is impossible, since this compound in chloroform or carbon tetrachloride starts to absorb light appreciably only at 295 mμ and lower, and at relatively high concentrations. Preliminary tests showed that it is possible to develop a photometric determination of cadmium, by converting its diethyldithiophosphate into the intensely colored copper diethyldithiophosphate and measuring the optical density of a solution of the latter in an organic solvent. It has been established that cadmium diethyldithiophosphate, on being dissolved in chloroform or carbon tetrachloride, interacts with cupric sulfate in aqueous solution (on shaking):

$$[(C_2H_5O)_2PSS]_2Cd + Cu^{2+} = [(C_2H_5O)_2PSS]_2Cu + Cd^{2+}.$$

SUMMARY

Cadmium diethyldithiophosphate $[(C_2H_5O)_2PSS]_2Cd$ answers all the requirements for a cadium compound which is readily precipitated, and is suitable for the gravimetric determination of this metal. A fairly rapid method has been developed for the gravimetric determination of cadmium in the presence of zinc, and also in the presence of nickel, cobalt, manganese, aluminum, iron, chromium, magnesium, the alkaline-earths, and the alkali metals. The method should find application for the analysis of natural and industrial products.

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THE USE OF SODIUM PARA-AMINOBENZOATE FOR THE TITRIMETRIC DETERMINATION OF CADMIUM

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Despite the existence of a considerable number of methods for the quantitative determination of cadmium [1-7], analysts frequently have to resort to the gravimetric sulfate method which, although characterized by accuracy, is very long and is not suitable for the determination of cadmium in a mixture of cations. In recent years complexometric methods of determining cadmium have become increasingly important.

During a study of the effect of substituents on the solubility of the benzoates, it was found that cadmium salts form a sparingly soluble compound with sodium para-aminobenzoate. This fact served as a basis for developing a quantitative method of determining cadmium. Essentially the method consists of the preliminary precipitation of cadmium by means of sodium para-aminobenzoate, and the subsequent bromatometric determination of cadmium in the precipitate on the basis of the para-aminobenzoic acid.

Before establishing the conditions for carrying out the method, the composition of the precipitate obtained by precipitating cadmium with sodium para-aminobenzoate was determined.

The precipitate was prepared by precipitating cadmium from a 0.3 M solution of cadmium acetate with a threefold excess of sodium para-aminobenzoate. The precipitate was washed 4 times with water, and dried at 120° to constant weight (this temperature ensures preparation of the anhydrous salt). Well known analytical reactions were used for detecting cadmium ions and para-aminobenzoic acid in the precipitate. Cadmium was determined quantitatively in the precipitate by dissolving an aliquot of the precipitate, which had been heated to constant weight at 120°, in 0.8 N sulfuric acid; the cadmium was then precipitated with hydrogen sulfide and determined gravimetrically as the sulfate [8]. The results of these determinations are given in Table 1.

TABLE 1

Wt. of prec., in g	$CdSO_4$ found, in g	Cd found	
		in g	in %
0.5160	0.2774	0.1501	29.0
0.5086	0.2714	0.1463	28.8
0.5010	0.2668	0.1439	28.7
0.5174	0.2780	0.1499	29.0
0.4978	0.2678	0.1444	29.0
		Mean	28.9

TABLE 2

Wt. of prec., in g	Para-aminobenzoic acid found	
	in g	in %
0.5088	0.3607	70.9
0.5076	0.3568	70.3
0.5080	0.3687	70.6
0.5052	0.3568	70.6
0.4154	0.2936	70.7
	Mean	70.6

For the quantitative determination of para-aminobenzoic acid, the exact amount of the product dried to a constant weight was dissolved in 1 N hydrochloric acid in a 100-ml standard flask. The para-aminobenzoic acid was determined bromatometrically in 25 ml of this solution. The results of these determinations are given in Table 2.

Found	28.9% Cd and 70.6% n-$H_2NC_6H_4COOH$
Calculated for $(H_2NC_6H_4COO)_2Cd$	29.2% Cd and 70.8% n-$H_2NC_6H_4COOH$

Results for the determination of the water of crystallization showed that cadmium para-aminobenzoate crystallizes with three molecules of water. Thus, the precipitate obtained during the interaction of cadmium salts with sodium para-aminobenzoate has the following composition:

$$(H_2NC_6H_4COO)_2Cd \cdot 3H_2O.$$

In order to study the effect of the amount of precipitant on the results of the cadmium determinations, precipitation was produced by various amounts of 0.3 M sodium para-aminobenzoate in 10 ml of cadmium acetate (0.003709 g Cd in 1 ml). After standing for 10 minutes the precipitate was filtered and then washed 4 times with water. The precipitate was dissolved in 50 ml 1 N hydrochloric acid, and the cadmium determined bromatometrically on the basis of para-aminobenzoic acid.

The results of these experiments are given in Table 3.

TABLE 3

(0.03709 g Cd taken)

Am't of 0.3 M sodium para-aminobenzoate, in ml	Molecular ratio of Cd to sodium para-aminobenzoate	Cd found, in g	Difference, in Cd, in g
1.5	1 : 1.3	Insignificant deposition of precipitate	
2.5			
3	1 : 2.2	0.03163	—0.00546
4	1 : 2.6	0.03373	—0.00336
5	1 : 3.5	0.03624	—0.00085
10	1 : 4.4	0.03624	—0.00085
25	1 : 9	0.03639	—0.00070
	1 : 22	0.03653	—0.00056

Thus, precipitation of cadmium starts at a molar ratio of cadmium to sodium para-aminobenzoate of 1 : 1.3. Complete precipitation is achieved at a ratio of 1 : 3.5. Excess of reagent has no effect on the accuracy of the results obtained.

In order to determine the time necessary for formation of the precipitate, 25 ml of a 0.3 M solution of sodium para-aminobenzoate was added to 20 ml of cadmium acetate solution containing 0.007200 g Cd per ml. The precipitates were allowed to stand for various time intervals. Cadmium was then determined in the precipitates by the method described above.

These tests showed that the length of time for which the precipitate is allowed to stand has no effect on the accuracy of the results. The precipitate settles out completely in the course of 10-15 minutes, and is readily filtered.

In order to study the loss of cadmium on washing with water, cadmium was precipitated from 20 ml of a solution of cadmium acetate (0.007200 g Cd per ml) by 25 ml of 0.3 M sodium para-aminobenzoate. After ten minutes standing the precipitate was transferred to a filter and washed with water. 4-6 ml of water was used for each washing, the precipitate was finally dissolved in 50 ml of 2 N HCl in a 100-ml standard flask and the volume made up to the mark with water. Cadmium was then determined bromatometrically in 25 ml of this solution.

The results of these experiments are given in Table 4.

These results show that low values are obtained when the precipitate is washed repeatedly with water. Washing with 70° alcohol gives completely acceptable results (Table 5).

Precipitation of cadmium is quantitative in the pH range 2-6.5.

The experimental results obtained enabled us to develop a method for the titrimetric determination of cadmium by means of sodium para-aminobenzoate.

An aliquot of the cadmium salt (0.1-0.15 g Cd) was dissolved in 15-20 ml of water, 25 ml of 0.3 M sodium para-aminobenzoate was added and the precipitate formed allowed to stand for 10-15 minutes. The precipitate was then transferred to a filter and washed 4-5 times with 70° alcohol. The precipitate was washed off the filter by means of 20-30 ml of 2 N hydrochloric acid into a 100-ml standard flask, and the volume made up to the mark with water. To 20-25 ml of this solution, contained in a flask, was added 25-30 ml of 1 N hydrochloric acid, followed by 0.5 g of potassium bromide; then 0.1 N $KBrO_3$ solution was added until the yellow color of bromine was observed; 5 ml of $KBrO_3$ solution was then added in excess. The whole was thoroughly mixed and 0.1 N arsenious acid added until the yellow color disappeared. Excess arsenious acid was titrated with potassium bromate in the presence of indigo carmine or methyl orange.

TABLE 4

(0.1440 g Cd taken)

No. of water washes	Cd found, in g	Difference in Cd, in g
3	0.1467	+0.0027
4	0.1427	−0.0013
5	0.1416	−0.0024
6	0.1414	−0.0026
10	0.1393	−0.0046

TABLE 5

(0.1440 g Cd taken

No. of alcohol washes	Cd found, in g	Difference in Cd, in g
3	0.1469	+0.0029
4	0.1457	+0.0017
5	0.1435	−0.0005
6	0.1435	−0.0005
10	0.1435	−0.0005

TABLE 6

Wt. of Cd $(CH_3COO)_2$, in g	Cd found		Wt. of $Cd(CH_3COO)_2$, in g	Cd found	
	in g	in %		in g	in %
0.2844	0.1205	42.36	0.2073	0.0873	42.57
0.3190	0.1354	42.43	0.3030	0.1289	42.55
0.3052	0.1289	42.33	0.3012	0.1276	42.36
0.4738	0.2006	42.37	0.4014	0.1698	42.32
0.4804	0.2036	42.39	0.4236	0.1788	42.22
	Mean	42.37		Mean	42.40

TABLE 7

Cd taken, in g	Cd found, in g	Difference in Cd	
		in g	in %
	Cadmium iodide		
0.0498	0.05001	0.00021	+0.4
0.0498	0.05058	0.00078	+1.5
0.0498	0.05001	0.00021	+0.4
	Cadmium chloride		
0.1242	0.1234	0.0008	−0.6
0.1242	0.1228	0.0014	−1.1
0.1242	0.1237	0.0005	−0.4
	Cadmium nitrate		
0.1064	0.1062	0.0002	−0.2
0.1064	0.1056	0.0008	−0.8
0.1064	0.1059	0.0005	−0.5

TABLE 8

(0.1440 g Cd taken)

Zn taken, in g	Cd found, in g	Difference in Cd, in g
0.07	0.1430	−0.0010
0.07	0.1422	−0.0018
0.07	0.1430	−0.0010
0.7	0.1435	−0.0005
0.7	0.1435	−0.0005
0.7	0.1430	−0.0010

1 ml of 0.1 N $KBrO_3$ corresponds to 0.001405 g Cd.

Using this method, the cadmium content of cadmium acetate (analytical grade GOST 7385/539 was determined. Cadmium was also determined gravimetrically in the same salt by the sulfate method.

The results given in Table 6 show that the accuracy of the proposed method lies within the limits of accuracy of the gravimetric sulfate method. We also checked on the possibility of using this method for other cadmium salts (the nitrate, chloride, and iodide). For this purpose solutions of these salts were prepared and their cadmium content determined both gravimetrically and by the proposed method.

The results obtained are given in Table 7. They show that the method suggested can be used for the determination of cadmium in its acetate, nitrate, chloride, and iodide.

Determination of Cadmium in the Presence of Zinc

During a study of the solubility of the substituted benzoic acids it was found that zinc is not precipitated by sodium para-aminobenzoate. For the determination of cadmium in the presence of various amounts of zinc, solutions of zinc acetate of known concentration were prepared. Known amounts of the zinc acetate solution were added to a cadmium acetate solution (the cadmium concentration was established gravimetrically). Cadmium was then determined quantitatively in this mixture by the method described above. The results obtained are given in Table 8.

This table shows that satisfactory results can be obtained during the determination of cadmium in the presence of zinc at a cadmium to zinc ratio of up to 1:5.

SUMMARY

A new titrimetric method has been developed for the determination of cadmium in the presence of zinc.

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A NEPHELOMETRIC DETERMINATION OF ZINC BY MEANS OF DIANTIPYRYLMETHYLMETHANE

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Some pyrazolone derivatives, in particular diantipyrylmethylmethane, are very sensitive reagents for zinc in the form of $[Zn(SCN)_4]^{2-}$ (under certain conditions). This anion gives sparingly soluble compounds with many organic cations of the ammonium type, for example benzoquinoline ($C_{13}H_9NH^+$), pyramidone ($C_{13}H_{17}ON_3H^+$) [2]. Iatsimirskii [3] has established that for precipitating anions with large ionic radius one should use cations with fairly large radii. Kuznetsov [4] has found solid phase reactions for $[Zn(SCN)_4]^{2-}$ with colored organic bases.

The present article contains a description of the synthesis and properties of the tetrathiocyanato zincate of diantipyrylmethylmethane; the optimum conditions for the nephelometric determination of zinc by means of this reagent are also described.

Preparation of Diantipyrylmethylmethane Tetrathiocyanatozincate

This compound was prepared by the interaction of 0.5 N zinc chloride, 2 N ammonium thiocyanate, and a 2% alcoholic solution of diantipyrylmethylmethane acidified with hydrochloric acid. Equal volumes of all three solutions (100 ml each) were poured together and the mixture heated almost to the boiling point. On cooling, a precipitate separated out which was recrystallized from alcohol acidified with hydrochloric acid.

Analysis of the compound prepared

0.1960 g of material; 0.0268 $Zn_2P_2O_7$
0.1864 g of material; 0.0254 $Zn_2P_2O_7$
0.0916 g of material; 0.0544 AgSCN
0.0906 g of material; 0.0534 AgSCN

Found %: Zn 5.87; 5.85; SCN 20.78, 20.62. Calculated %: Zn 5.91; SCN 21.03.

The analytical results indicated that the reaction can be written as follows:

$$2C_{11}H_{11}ON_2 \cdot CH(CH_3) \cdot C_{11}H_{11}ON_2 + ZnCl_2 + 2HCl + 4NH_4SCN =$$
$$= [C_{11}H_{11}ON_2 \cdot CH(CH_3) \cdot C_{11}H_{11}ON_2H]_2[Zn(SCN)_4] + NH_4Cl.$$

The properties of this compound are listed in Table 1.

A characteristic of this compound is its capacity to form a stable turbidity in very dilute aqueous solutions. On the basis of the properties of this compound, a photonephelometric method of determining zinc was developed. The sensitivity of this reagent for the detection of zinc is 0.09 μg of Zn/ml.

Photonephelometric Determination of Zinc

1. Preparation of Diantipyrylmethylmethane Hydrochloride [5]. 5 g of antipyrine was dissolved in a small amount of water, and 1-2 ml of hydrochloric acid sp. gr. 1.19, and 1-2 ml of acetaldehyde added. The

mixture was heated on a water bath for 30-40 minutes, when a crystalline mass was formed. The material was recrystallized from water. It was finally dried in a desiccator.

TABLE 1

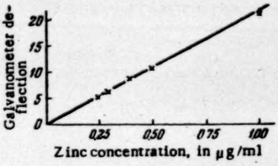
Properties of $[C_{11}H_{11}ON_2 \cdot CH(CH_3) \cdot C_{11}H_{11}ON_2 \cdot H]_2[Zn(SCN)_4] + NH_4Cl$	
Color	White
Solubility	
In water at 15°	0.12 : 100
In alcohol at 15°	0.15 : 100
In ether at 15°	Insoluble
Behavior with $FeCl_3$	One drop of $FeCl_3$ solution gives a red color of $Fe(SCN)_3$
Behavior with $AgNO_3$	A white precipitate of AgSCN is formed in a nitric acid medium
Behavior with $K_4[Fe(CN)_6]$	A white precipitate $K_2Zn_3[Fe(CN)_6]_2$ is formed
Behavior with NaOH	No precipitate formed
Melting point	127-129°

2. Preparation of a Solution of the Reagent. 1.52 g of ammonium thiocyanate was dissolved in 99 ml of twice-distilled water. To this solution was added, with stirring, 1 ml of a 2% alcoholic solution of diantipyrylmethylmethane; when this was done, a weak turbidity sometimes developed; this was removed by filtering the solution through a normal filter.

TABLE 2

Relation between Zinc Concentration of the Solution and the Galvanometer Readings

Test no.	Zinc conc. in μg Zn in 1 ml test solution	Galvanometer deflection
1	0.25	5.5
2	0.40	9.0
3	0.50	11.0
4	0.70	15.0
5	1.00	21.2



Relation between zinc concentration of the solution and galvanometer readings.

3. Determination of Zinc in Diantipyrylmethylmethane Solutions. Into one cell of a Bendt type photocolorimeter was placed 5 ml of test solution, 0.25 ml of 1 N hydrochloric acid, 0.75 ml of water, 0.03 g of ascorbic acid, 0.05 g of thiourea, and 9 ml of reagent, while a control solution was poured into the other cell.

TABLE 3

Ions	Conc. of ions, μg per ml			
	Solutions			
	№ 1	№ 2	№ 3	№ 4
Magnesium	90	—	9	—
Aluminum	19	—	1.9	—
Copper	1	1	—	—
Iron Fe^{3+}	—	10	—	—
Manganese	—	—	100	10

On the basis of the results obtained (Table 2), a curve relating zinc concentration to galvanometer readings was drawn (Fig).

Four solutions were prepared for the determination of zinc in the presence of Mg^{2+}, Al^{3+}, Cu^{2+}, Fe^{3+}, and Mn^{2+} (Table 3). The zinc concentration was varied over the range 0.25 μg to 1.0 μg per ml.

The reagent solution did not give a turbidity with solutions of the ions indicated in Table 3 over a period of several hours. The experimental conditions used for the determination of zinc in the presence of these metals were the same as those in the previous experiments. Results of these determinations are given in Table 4.

The presence of Group I and II cations does not interfere with zinc determination; manganese (100 μg), copper (1 μg), nickel, and cobalt (5 μg each) per ml of solution do not interfere. At low concentrations, ferric iron is reduced to the divalent state by means of ascorbic acid or hydroquinone. Cupric ions are converted into a colorless complex with thiourea when they are present in amounts greater than 1 μg per ml.

TABLE 4

Determination of Zinc in the Presence of Other Metals (10 ml of each of the solutions given in Table 3 were taken)

Test no.	Zinc conc. of test soln., μg per ml	Zinc content found μg per ml	Expt. error, μg per ml	Test no.	Zinc conc. of test soln., μg per ml	Zinc content found μg per ml	Expt. error, μg per ml
1	0.25	0.27	+0.02	6	0.25	0.24	−0.01
2	0.75	0.73	−0.02	7	0.50	0.53	+0.03
3	1.00	1.01	+0.01	8	1.00	1.02	+0.02
4	0.25	0.24	−0.01	9	0.25	0.27	+0.02
5	0.75	0.73	−0.02	10	0.75	0.73	−0.02

The method described has been used for the analysis of alloys, tap water, and spring water.

Determination of Zinc in Alloys

0.1 g of the alloy "elektron" containing 85% Al, 14.17% Mg, 0.29% Mn, 0.08% Cu, and 0.46% Zn was dissolved in a few ml of hydrochloric acid sp.gr 1.03 contained in a quartz beaker. When solution was complete, the liquid was transferred to a 1-liter standard flask. The solution was made up to the mark with twice-distilled water. For the zinc determination 5 ml of this solution was taken, and 0.25 ml of 1.0 N HCl, 0.03 g of ascorbic acid, 0.05 g of thiourea, and 9 ml of reagent solution added to it. After standing for 15 minutes the solution was transferred to the photocolorimeter cell. The other cell was filled with control solution (this solution contained all the components listed above but contained 5 ml of water instead of test solution). The following results were obtained in a series of tests in which zinc was added to the test solutions (Table 5).

TABLE 5

Determination of Zinc in the Alloy "Elektron" (composition 85% Al, 14.17% Mg, 0.46% Zn, 0.29% Mn, 0.08% Cu; sample weight 0.1 g)

Zn content of alloy, mg	Zinc added, mg	Total zinc found, mg	Theor. Zn content, mg	Error, in mg
0.46	—	0.44	0.46	−0.02
0.46	0.30	0.70	0.76	−0.06
0.46	0.40	0.82	0.86	−0.04

The experimental error for the determination of zinc did not exceed ± 10%.

Determination of Zinc in Tap Water*

To 10 ml of test water contained in a platinum basin was added 0.5 ml of sulfuric acid sp. gr. 1.84. The solution was carefully evaporated until fumes of sulfur trioxide had ceased to be evolved. 0.25 ml of 1.0 N HCl, 9.75 ml of twice-distilled water, and 0.03 g of ascorbic acid or 0.2 g of hydroquinone for reducing any iron present, were added to the dry residue obtained by evaporation.

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* V. Babushkin and V. Lopatina, students at the Perm Medical Institute, took part in the determination of zinc in tap and spring water.

The contents of the platinum dish were mixed and filtered through a dry filter (treated with twice-distilled water beforehand). To 5 ml of this filtrate, 9 ml of the zinc reagent was added, and the liquid mixed by pouring from one tube into another; the final mixture was allowed to stand for 15 minutes and the zinc determined nephelometrically.

TABLE 6

Determination of Zinc in Tap Water

Tap water source	Zn found, mg/liter	Zn added, mg/liter	Total Zn found, mg/liter	Theor. Zn content, mg	Expt. error, mg
Factory A	0.24	—	0.24	—	—
	0.24	0.25	0.55	0.49	+0.06
Factory B	0.22	—	0.22	—	—
	0.22	0.25	0.48	0.47	+0.01
Factory C	0.35	—	0.35	—	—
	0.35	0.25	0.55	0.60	—0.05
Factory D	0.66	—	0.66	—	—
	0.66	0.25	0.90	0.91	—0.01

When the water contained organic material, 10 ml of the water was placed in a quartz Kjeldhal flask, and 1 ml of sulfuric acid sp. gr. 1.84 and 1 ml of hydrogen peroxide added. The mineralizate was transferred to a platinum dish and the flask rinsed out a few times with twice-distilled water; the solution was then evaporated to remove excess sulfuric acid. The procedure followed subsequently is the same as that outlined above. The experimental results are given in Table 6.

Determination of Zinc in Spring Water

Since the test drinking water (particularly the spring water) contained such small amounts of zinc, 200-250 ml of water was taken for analysis instead of 10 ml. The water was evaporated in a platinum dish and the procedure outlined above for tap water then followed.

TABLE 7

Determination of Zinc in Spring Water

Place of sampling	Zinc found, μg/liter
Spring No. 1, Egoshikh	10.0
No. 2	8.4
No. 3	8.5
No. 4	12.2
No. 5	12.5
Staryi Polskii village	100.0

The results obtained are given in Table 7.

SUMMARY

1. A new compound $[C_{24}H_{26}O_2N_4H]_2[Zn(SCN)_4]$ has been prepared by the interaction of zinc with diantipyrylmethylmethane and thiocyanate in acid media.

2. Group I and II cations, aluminum, and manganese in amounts of 100 μg, trivalent iron in amounts

of 10 μg, and copper in amounts of 1 μg per ml of solution, do not interfere with determination of zinc in the form of the above compound by a nephelometric method.

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A NEW METHOD FOR THE FLUORIMETRIC DETERMINATION OF GALLIUM

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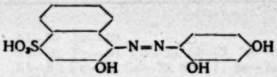
Several reagents have been suggested in the literature for the fluorimetric determination of gallium; they include: 8-hydroxquinoline [1-3], 5,7-dibromohydroxyquinoline [4], morine, and cupferron [5], salicylidene – ortho-aminophenol [6], and dyes of the solochrome group – solochrome red ERS, and solochrome black WDFA [7]. Solochrome group dyes, for example solochrome 6BFA [8,9], have also been described earlier as fluorescent indicators for the qualitative detection of gallium.

The methods described have a fairly low sensitivity (the limit of identification is 0.1 γ of gallium), and some of them, i.e. the most widely used one 8-hydroxyquinoline, are severly hampered by iron, separation of traces of which is not always easy and convenient.

In a search for a more specific and sensitive method of determining submicrogram amounts of gallium, we tried out a number of reagents suggested for this element by Poluektov and Kiseleva [10]. The most sensitive of them proved to be a dye – also of the solochrome group – 1,3-dihydroxybenzene - <4-azo-1> -2'-naphthol-4'-sulfonic acid (henceforth called sulfonaphthol-azoresorcinol), obtained by coupling diazotized 1-amino-2-naphthol-4-sulfonic acid with resorcinol.



This reagent, in an aqueous-alcohol solution at pH 3, gives in ultraviolet light a bright orange luminescence with gallium. By adding to 1 ml of a gallium solution containing 0.2 ml of 0.2 N hydrochloric acid, 0.2 ml of a chloride-acetate buffer (ph 3.0), 2 ml of 95% alcohol purified by distillation, and 0.2 ml of a 0.01% alcoholic solution of reagent, it is possible to detect as little as 0.01 γ of gallium on the basis of the weak orange-red luminescence when comparison is made with a blank. A series of solutions prepared in this way, and containing: 0.00–0.02–0.05–0.10–0.15–0.20–0.25–0.30–0.40–0.50 γ of gallium, form a well-defined standard scale, in which the intensity of the luminescence is proportional to increasing gallium concentration. The specificity of this reaction is better than that with 8-hydroxyquinoline. Table 1 contains data on the permissible amount amounts of certain elements in the test solution.

When using sulfonaphtholazoresorcinol for the quantitative determination of gallium in various natural materials, large amounts of accompanying metals should be removed. In many cases one can resort to the usual method of removing gallium – extraction of this element as its trichloride with ether. Such a separation, however, may prove insufficient during the analysis of samples containing tin, antimony, large amounts of copper, and other heavy metals, since certain amounts of these elements will also be extracted and get into the final solution. Consequently, in the given instance, we used a double separation: first, the heavy metals were removed by cementation on metallic cadmium [1], during which, in addition, iron was reduced to the divalent state; then the gallium was removed by extraction from divalent iron, aluminum, titanium, etc.

TABLE 1

Permissible Amounts of Various Elements during Gallium Detection

Element	Permissible amount, in γ	Element	Permissible amount, in γ
Aluminum	2	Zinc	2
Iron (III)	2	Antimony (III)	8
Iron (II)	10	Tin (IV)	15
Indium	100 *	Germanium	200
Titanium	10 *	Arsenic	15
Molybdenum	2	Phosphorus	2000
Thallium (I)	500	Calcium	10 *
Vanadium	1 *	Magnesium	10 *

*Large amounts of these elements were not tested.

Table 2 contains results for the determination of gallium in synthetic mixtures of various salts. Determination was carried out as described later. It is clear from Table 2 that when this analytical procedure is adopted, completely satisfactory results are obtained.

During determination of the gallium content of bauxites, silicates, sulfide ores, and waste materials from nonferrous metals, etc.the following method of getting the test material into solution was used. Bauxites were fused with potassium pyrosulfate, and the melt dissolved in water and hydrochloric acid. Silicates were broken down first with hydrofluoric and sulfuric acids, and then fused with potassium pyrosulfate as in the case of bauxites. Sulfide ores and nonferrous waste were given an acid treatment. Subsequently, in all cases cementation of the heavy metals on cadmium was carried out, followed by extraction of gallium chloride with ether. After removal of the ether, gallium was determined by means of sulfonaphtholazoresorcinol. Table 3 contains the results obtained for determination of gallium in bauxites, silicates, and wastes from zinc production. Table 3 also contains results obtained during determination of gallium which had been added to the test material before its break down.

TABLE 2

Determination of Gallium in Synthetic Mixtures

Ga added, in γ	Added, in mg	Ga found in γ	Difference in γ
50	—	49	—1
50	Al—30. Fe—40	50	0
50	Al—30. Fe—40. Cu—25. Sb—2. Sn—2	46	—4
12	Al—30. Fe—40. Cu—25. Sb—2. Sn—2. Mo—1	11.5	—0.5
12	Al—30. Fe—40. Cu—25. Sb—2. Sn—2. Mo—1. Zn—30. Ph—40. As—5	11.4	—0.6

During determination of gallium in coal, combustion may lead to partial volatilization of gallium. Accordingly, we tried out the possibility of rapid ashing of coal which would exclude loss of gallium. Of the various methods which we tried, the one that gave the most reliable results was heating the test material with a mixture of calcium oxide and nitrate. Thanks to the high sensitivity of the fluorimetric method involving sulfonaphtholresorcinol, it was sufficient to take for analysis an aliquot of 0.5−1 g; this meant that ashing could be speeded up. Calcination with calcium oxide of the residue obtained after ashing the coal favors decomposition of the silicate part of the coal, and the conversion of all the ashed part of the coal into a form which is soluble in acid. After ashing and calcining, the residue was dissolved in hydrochloric acid and the interfering elements removed by cementation on cadmium; gallium was then extracted as its trichloride, as in the analysis of ores.

Table 3 contains the results obtained for gallium determination in two samples of coal. Here, as in the case of ore analysis, some samples were analyzed after addition of gallium to the sample of coal before the treatment described above.

The fluorimetric method described also proved suitable for the determination of gallium in certain metals,

TABLE 3

Determination of Gallium in Ores, Coal, and Wastes

Test material	Sample wt., in g	Ga added, in γ	Ga found, plus that added	
			in τ	in %
Bauxite	0.2	—	8.2	0.0041
	0.2	—	8.8	0.0044
	0.3	—	12.5	0.0042
	0.2	8	16.4	0.0082
	0.2	10	18.6	0.0093
Zinc concentrate	0.5	—	2.5	0.0005
	0.5	—	3.0	0.0006
	0.5	2	4.5	0.0009
	0.5	2	5.0	0.0010
Lead concentrate	1.0	—	0.6	0.00006
	1.0	—	0.5	0.00005
	1.0	0.5	1.1	0.00011
	1.0	6.0	6.7	0.00067
Sulfide-silicate ore	0.5	—	8.3	0.0017
	0.5	—	8.0	0.0016
	0.5	12	20.0	0,0040
Silicate plus sulfides(flotation tailings)	0.5	—	9.3	0.0019
	0.5	—	10.0	0.0020
	0.5	6	16.0	0.0032
	0.5	12	22.5	0.0045
Copper-cadmium cake	0.2	—	2.0	0.0010
	0.2	1	3.0	0.0015
	0.2	3	5.0	0.0025
Zinc cake	0.1	—	3.0	0.0030
	0.2	—	6.8	0.0034
	0.2	6	13.0	0.0065
Coal I	1.0	—	2.0	0.00020
	1.0	—	1.7	0.00017
	1.0	2	3.7	0.00037
	1.0	3	4.7	0.00047
Coal II	1.0	—	0.2	0.000020
	1.0	0,4	0.56	0.000056

in particular, in aluminum, zinc, and lead. Aluminum can be dissolved in hydrochloric acid. Zinc can also be dissolved in hydrochloric acid.

In both instances, where it is necessary to dissolve metallic tailings, nitric acid must be added. Lead is dissolved in nitric acid which is subsequently removed by evaporation with hydrochloric acid. In order to remove nitric acid completely, the residue should be evaporated with hydrochloric and formic acids. The heavy metals are then removed by cementation on cadmium, while gallium is extracted with ether as for ore analysis. Table 4 contains the results obtained during the analysis of gallium in samples of aluminum, zinc, and lead.

TABLE 4

Determination of Gallium in Aluminum, Zinc, and Lead

Sample	Sample wt.	Ga added in γ	Ga found, plus that added	
			in τ	in %
Technical aluminum, powder	0.2	—	25	0.0125
	0.1	—	13	0.0130
Pure aluminum, Duzharden factory, Dusseldorf	0.1	—	0.05	0.00005
	0.2	—	0.12	0.00006
	0.1	0.2	0.24	0.00024
Pure granulated zinc, "arsenic free"	0.5	—	0	0
	0.5	2.5	2.5	0.00050
	0.5	5.0	4.8	0.00096
Pure granulated lead	0.5	—	0	0
	0.5	2.5	2.5	0.0005
	0.5	4.0	4.0	0.0008

Analytical Procedure

Reagents: 1. Diethyl ether, free from peroxides, equilibriated with 6 N hydrochloric acid. 2. Ethanol, 96% purified by distillation. 3. Hydrochloric acid, 6 N, saturated with ether. 4. Hydrochloric acid, 0.2 N,

obtained by dilution with twice-distilled water of concentrated acid, obtained in turn by saturation of twice-distilled water with gaseous hydrogen chloride. 5. Chloracetate buffer (pH 3.0). A mixture of equal volumes of 0.5 M monochloroacetic acid and ammonium monochloroacetate. 6. Titanium trichloride, 20% solution in 6 N hydrochloric acid. This can be prepared from powdered titanium metal. 7. Water – twice-distilled – prepared in a quartz distillation apparatus. The twice-distilled water was only used in the later stages of the analysis for dissolving the residue after evaporation of the ether extract, and for preparing reagent. 4. In all other cases, ordinary distilled water was used. 8. Sulfonaphtholazoresorcinol, 0.01% alcoholic solution. 9. Calcium nitrate, prepared by dissolving 50 g of the tetrahydrate in 100 ml solution.

Dissolving the Test Material

a) Bauxite: 0.2 g of material was fused in a Pt crucible with 4 g of potassium pyrosulfate; after cooling, the melt was dissolved in 15 ml of water and 15 ml of concentrated hydrochloric acid on heating.

b) Silicates: 0.1–0.3 g of silicate was broken down with 5-10 ml of hydrofluoric acid and 0.5 ml of concentrated sulfuric acid. After removal of H_2F_2 by evaporation, 4 g of potassium pyrosulfate was added to the residue, and the procedure given for bauxite subsequently followed. Micas were fired before grinding and decomposing.

c) Sulfide Ores and Nonferrous Wastes. 0.1–1.0 g of sample (depending on the amount of gallium expected) was heated in a 100-ml beaker covered with a watch glass, with 10 ml of concentrated hydrochloric acid until hydrogen sulfide had ceased to come off. Heating was then continued while nitric acid was added in 0.2-ml lots (total amount 0.6 to 3 ml) until the test sample had broken down completely. The watch glass was next removed and the contents evaporated to dryness with hydrochloric acid added in two 2-ml lots. Finally, the residue was evaporated with a third 2-ml lot of hydrochloric acid to which 0.5 ml of 85% formic acid was added. The residue was dissolved on heating in 20 ml of 3 N hydrochloric acid.

In the case of poor sulfide ores, or of samples with a high silicate content, the latter must also be broken down. In such cases the test was broken down first with nitric acid, and then with H_2F_2 and H_2SO_4; the procedure followed subsequently was the same as that described for silicate analysis.

d) Aluminum, Zinc, Lead: 0.1–0.3 g of aluminum, or 0.1–0.5 g of zinc was dissolved on heating in 3 N hydrochloric acid. After the metal had dissolved, 0.5 ml of concentrated nitric acid was added and the mixture evaporated to dryness. The residue was evaporated twice with hydrochloric acid, and then with hydrochloric plus formic acid as for sulfide analysis.

Lead (0.2–0.5 g) was dissolved in nitric acid, after which the solution was evaporated to dryness; the residue was then evaporated a few times with hydrochloric acid, and finally with hydrochloric plus formic acid. The residue obtained by evaporation was dissolved in 20 ml of 3 N hydrochloric acid.

e) Coal. 1-2 g of finely ground coal was mixed in a platinum basin with 0.5 g of calcium oxide and 5 ml of calcium nitrate solution. The mixture was evaporated to dryness and dried on a sand bath. It was then heated in a muffle furnace, first at 400-500° and then, after the main bulk of the coal had burnt off, at 800° until all the carbon particles had been removed. In order to speed up the process, the lumps of burning material were broken up with a rod. The residue left after combustion was transferred to a 100-ml beaker; there it was moistened with water, and dissolved in 10 ml of concentrated hydrochloric acid. The solution was evaporated to dryness and the residue dissolved in 20 ml of 3 N hydrochloric acid.

Isolation of Gallium. To the solution obtained by any one of the techniques described above, without filtering it, was added 0.5-2 g of cadmium metal in the form of spongy metal or fine turnings, and the whole mixed for 5-10 minutes until the iron had been reduced (the solution becomes colorless), and the heavy metals had been deposited. When the iron was not completely reduced, the mixture was warmed slightly and again agitated for a few minutes. Completeness of removal of the heavy metals was controlled by addition of fresh cadmium turnings – fresh turnings should not become covered with a dark film. The solution finally obtained was filtered through a cotton wool plug washed with 3 N hydrochloric acid, into a separating funnel washed out with 6 N hydrochloric acid. To this filtrate was added 0.2 ml of titanium trichloride and the whole left to stand for 1 minute; 13 ml of 12 N hydrochloric acid was then added, and the solution extracted three times with ether – twice with 15 ml of ether, and the third time with 10 ml – the funnel being shaken for 1 minute each time. The combined ether extracts contained in another separating funnel were washed twice with 3-ml lots of 6 N hydrochloric acid. The washed extracts were poured into a 50-ml beaker containing 0.5 ml of a 10% solution of sodium chloride, and the ether carefully evaporated off; the residue was finally evaporated to dryness on a water bath. The residue was moistened with 0.5 ml 0.2 N hydrochloric acid and transferred to a 25-ml standard flask.

Determination. To 1 ml of the solution obtained, contained in a colorimeter tube, was added 0.20 ml of 0.2 N hydrochloric acid, 0.20 ml of 10% hydroxylamine solution, 0.20 ml of chloracetate buffer, 20 ml alcohol, and 0.20 ml sulfonaphtholazoresorcinol, and the whole mixed. After one hour the fluorescence of the solution was compared with the fluorescence of a series of standards prepared at the same time; the test tubes were examined against a black background in the filtered light of a mercury-quartz tube.

The standard series prepared covered the range 0.00-0.40 γ of gallium at intervals of 0.05 γ. A blank should be carried out, all the experimental procedure given above being followed for the blank.

When the gallium content of the sample is low, the residue left after evaporation of the ether can be dissolved in 10 ml or less of water rather than in 25 ml. In such cases, in preparing the standard series one must take into account the sodium chloride and hydrochloric acid content of the aliquot part of the solution taken for the determination.

SUMMARY

It has been shown that it is possible to use a reaction with 1,3-dihydroxybenzene-<4-azo-1>-2-napthol-4-sulfonic acid for the quantitative fluorimetric determination of gallium. On the basic of this reaction, a method has been developed for the determination of gallium in ores, coal, metals , and waste products of the nonferrous metal industry. The sensitivity of the method is as high as n × 10^{-5}% of gallium.

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DETERMINATION OF ZIRCONIUM BY MEANS OF AMMONIUM BENZENESELENINATE AND AMMONIUM NAPHTHALENESELENINATE

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Organic precipitants can be successfully used as well as inorganic reagents such as sodium phosphate, potassium iodate, and selenious acid, for the quantitative determination of zirconium, and for its separation from other elements. The most widely used methods are those involving precipitation with cupferron [1], and phenylarsonic and propylarsonic acids [2-4]. In recent years other precipitants have also been recommended, for example, mindalic acid [5-7] and its halogen derivatives [8], phthalic acid [9, 10] etc. All the reagents listed precipitate a certain limited number of elements, and the number of such elements can be restricted by using masking agents. A drawback of the precipitants is the fact that the compounds formed do not always correspond to the strictly stoichiometric formula, while coprecipitation of other elements is sometimes observed. As a result, the search for new organic reagents for zirconium and hafnium continues. Recently [11] benzenesulfinic acid $C_6H_5-SO_2H$ was suggested for the precipitation of zirconium, and for its separation from a number of other elements.

We have synthesized a large number of organic reagents containing the group $-SeO_2H$, which form sparingly soluble compounds with a number of quadrivalent elements (Ti, Zr, Hf, Ce^{IV}), and also with Nb and Ta [12]. The ones studied in greatest detail were benzene- and naphthalene- seleninic acids (and their ammonium salts). The present article contains descriptions of methods for determining zirconium and separating it from other elements.

The reagents $C_6H_5-SeO_2NH_4$ and $C_{10}H_7-SeO_2NH_4$ in strongly acid solutions of zirconium salts, form white amorphous precipitates, which on calcining give pure zirconium dioxide.

The limiting dilution at which precipitation of zirconium by means of the first reagent occurs is 1:1,000,000, while for the second reagent this limit is at 1:1,500,000.

The composition of the precipitates dried in air, according to analytical results approximates to the formula $ZrO(R-SeO_2)_2$; nevertheless, these compounds are not suitable for gravimetric use, accordingly, for the quantitative determination of zirconium, the precipitates are calcined and the residue of ZrO_2 weighed.

The variation in the composition of these compounds, as the variation in composition of a number of other compounds, is related to the tendency of zirconium salts, even in acid solution, to hydrolyze and also to form polymeric ions [13, 14].

In order to establish the optimum conditions for precipitating zirconium, we studied the effect of the concentration of various mineral acids. For this purpose, various amounts of nitric, hydrochloric, or sulfuric acids were added to a standard nitric acid solution of zirconium; the liquids were then diluted with water to 100 ml, and heated to the boiling point; precipitation of zirconium was effected by either ammonium benzeneseleninate or naphthaleneseleninate.

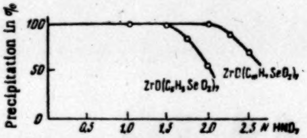
The solution plus precipitate was heated for 25-30 minutes, after which some macerated paper was added and, on cooling, the precipitate was filtered through a fine filter; the precipitate was washed with 0.1 N hydrochloric acid containing 0.4% of reagent, it was finally dried, and then calcined in a porcelain crucible at 800-900°.

On the basis of the results obtained (Fig. 1) the following optimum conditions for precipitation of zirconium were establsihed:

Concentration of nitric or hydrochloric acid	1.0 N
Concentration of ammonium benezeneseleninate	0.7%
Concentration of ammonium naphthaleneseleninate	0.5%

For quantitative precipitation of zirconium from sulfuric acid solutions, a higher concentration of precipitant is necessary, since in this case formation of complex anions of $[ZrO(SO_4)_2]^{2-}$ occurs.

Determination of Zirconium by means of Ammonium Benzene- and Naphthaleneseleninate in the Presence of Aluminum, Beryllium, the Rare Earths, and Trivalent Iron. Since aluminum, beryllium, and the rare earths are not precipitated by ammonium benzene- or naphthaleneseleninate, it was decided to check experimentally on the possibility of carrying out a quantitative determination of zirconium in the presence of the elements indicated. Trivalent iron is precipitated by ammonium benzene- or naphthaleneseleninate; nevertheless, in contrast to that of zirconium, the precipitate given by iron is readily soluble in mineral acids.



Effect of HNO_3 concentration on precipitation of zirconium as the benzene- and naphthaleneseleninates.

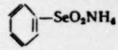
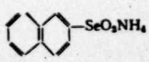
Results for the determination of zirconium in the presence of aluminum, beryllium, the rare earths, and trivalent iron are given in Table 1.

In the presence of large amounts of aluminum, beryllium, the rare earths, and iron, the precipitate is always contaminated by these elements; accordingly it is necessary to reprecipitate it.

Determination of Zirconium in the Presence of Titanium, Niobium, and Tantalum. Most elements are not precipitated in acid media by ammonium benzene- or naphthaleneseleninate and do not interfere with the determination of zirconium; exceptions are quadrivalent tin, titanium, niobium, and tantalum, which form similar precipitates in strongly acid solutions. Interference from the last three elements can be readily removed by addition of hydrogen peroxide, which forms complex compounds with these elements; hydrogen peroxide thereby prevents their precipitation, but does not affect the quantitative precipitation of zirconium. Tin should be removed beforehand by precipitation with hydrogen sulfide.

TABLE 1

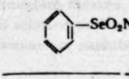
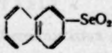
Determination of Zirconium in the Presence of Aluminum, Beryllium, the Rare Earths, and Trivalent Iron

Reagent	Taken, in mg					ZrO_2 found, in mg	Error, in mg
	Al_2O_3	BeO	Fe_2O_3	Σ r.e.	ZrO_2		
 —SeO_2NH_4	250.0	—	—	—	1.22	1.23	+0.01
	250.0	—	—	—	1.22	1.22	±0.00
	—	300.0	—	—	1.22	1.20	—0.02
	—	300.0	—	—	1.22	1.19	—0.03
	—	—	30.0	—	1.22	1.25	+0.03
	—	—	30.0	—	1.22	1.24	+0.02
	—	—	—	150.0	1.22	1.19	—0.03
	—	—	—	150.0	1.22	1.24	+0.02
 —SeO_2NH_4	250.0	—	—	—	1.22	1.20	—0.02
	250.0	—	—	—	1.22	1.21	—0.01
	—	—	30.0	—	1.22	1.24	+0.02
	—	—	30.0	—	1.22	1.22	±0.00
	—	—	—	150.0	1.22	1.25	+0.03
	—	—	—	150.0	1.22	1.25	+0.03

Precipitation of zirconium in the presence of hydrogen peroxide was carried out as follows. To the solution of the zirconium salt, 5 ml of 30% hydrogen peroxide was added, followed by 1.0 ml of 5-10 N hydrochloric acid,* the solution was then diluted with water to 100 ml and the zirconium precipitated with ammonium benzene- or naphthaleneseleninate.

TABLE 2

Determination of Zirconium by Precipitation with Ammonium Benzene- and Naphthaleneseleninate in the Presence of Hydrogen Peroxide

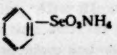
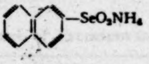
Reagent	ZrO_2 taken, in mg	ZrO_2 found, in mg	Error, in mg
	3.4	3.4	±0.0
	3.4	3.5	+0.1
	1.7	1.6	−0.1
	1.7	1.7	±0.0
	3.4	3.5	+0.1
	3.4	3.3	−0.1
	1.7	1.7	±0.0
	1.7	1.7	±0.0

For the determination of zirconium in the presence of titanium, niobium, and tantalum, the mixtures of oxides were fused with 10-12 times their amount of potassium pyrosulfate, and the melt dissolved in 3-5 ml of 30% hydrogen peroxide, 1-2 ml of sulfuric acid (1 : 1), and 40-50 ml water; the solution obtained was diluted with water to 100 ml and the zirconium precipitated with ammonium benzene- or naphthaleneseleninate.

The results obtained are given in Table 3.

TABLE 3

Determination of Zirconium in the Presence of Titanium, Niobium, and Tantalum

Reagent	Taken, in mg				ZrO_2 found, in mg	Error, in mg
	TiO_2	Nb_2O_5	Ta_2O_5	ZrO_2		
	17.0	—	—	1.7	1.6	−0.1
	17.0	—	—	1.7	1.8	+0.1
	—	14.0	—	1.7	1.7	±0.0
	—	14.0	—	1.7	1.6	−0.1
	—	—	12.0	1.7	1.8	+0.1
	—	—	12.0	1.7	1.6	−0.1
	17.0	—	—	1.7	1.8	−0.1
	17.0	—	—	1.7	1.6	−0.1
	—	14.0	—	1.7	1.8	+0.1
	—	14.0	—	1.7	1.7	±0.0
	—	—	12.0	1.7	1.6	−0.1
	—	—	12.0	1.7	1.8	+0.1

In the presence of large amounts of titanium, it is necessary, for its complete removal from zirconium, to reprecipitate the zirconium benzene- and naphthaleneseleninates; for this purpose the precipitate is washed with a small amount of water into the beaker in which the first precipitation was carried out and the precipitate treated with 5 ml of concentrated HNO_3 with gentle warming; the liquid is then diluted with water to 100 ml and the zirconium reprecipitated.

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*In strongly acid solutions, hydrogen peroxide in the course of time partially reduces the reagents to $(RSe)_2$.

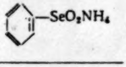
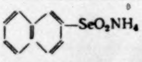
The completeness of the removal of zirconium from titanium was controlled by a photometric method involving hydrogen peroxide, while completeness of removal of zirconium from niobium and tantalum was controlled radiometrically, using the radioactive isotopes Zr^{95} and Niobium^{95}.

It was established that for a single precipitation of zirconium in the presence of titanium, niobium, and tantalum, in the quantities given in the table, less than 0.1 mg of the elements indicated could be found in the calcined residue of zirconium dioxide.

For objects with higher contents of niobium and tantalum, the benzene- and naphthaleneseleninate methods, like the phosphate and phenylarsonate methods, are unsuitable. In such cases, the precipitates of zirconium benzene- and naphthaleneseleninates contaminated with niobium and tantalum can, after calcination to give zirconium dioxide, be fused with potassium pyrosulfate, after which the melt is treated with 5% pyrogallic acid solution as described in [15]; the zirconium is then precipitated in the filtrate by means of ammonium benzene- or naphthaleneseleninate.

TABLE 4

Determination of Zirconium in Steel

Reagent	ZrO_2 added		ZrO_2 found		Error, in %
	in mg	in %	in mg	in %	
	3.59	1.44	3.59	1.44	±0.00
	3.59	1.44	3.60	1.44	±0.00
	7.18	2.88	7.17	2.88	±0.00
	7.18	2.88	7.20	2.89	+0.01
	3.59	1.44	3.58	1.44	±0.00
	3.59	1.44	3.56	1.43	—0.01
	7.18	2.88	7.16	2.87	—0.01
	7.18	2.88	7.21	2.89	+0.01

It should be pointed out that when precipitation of zirconium with ammonium benzene- or naphthaleneseleninate is carried out in the absence of hydrogen peroxide, the zirconium can be used as a collector for the isolation of small amounts of titanium, niobium, or tantalum. For this purpose a few milligrams of any zirconium salt is added to the test solution, and then precipitation effected with ammonium benzene- or naphthaleneseleninate; when such a procedure is followed, traces of titanium, niobium, and tantalum are coprecipitated with the zirconium. After filtration the precipitate is calcined and the residue fused with potassium pyrosulfate; titanium is then detected by the reaction with hydrogen peroxide, while niobium is detected as the thiocyanate [16], or niobium and tantalum are detected by means of pyrogallic acid [17].

Results for the determination of zirconium in steel and evdialite are given in Tables 4 and 5.

TABLE 5

Determination of Zirconium in Evdialite

ZrO_2 found, in %		
The phenylarsonate method	Benzeneseleninate method	The naphthaleneseleninate method
10.32	10.23	10.19
10.28	10.30	10.28
10.41	10.45	10.36

SUMMARY

Ammonium benzeneseleninate and ammonium naphthaleneseleninate are suggested as reagents for the determination of zirconium, and for its separation from a number of other elements (aluminum, beryllium, the rare earths, titanium, niobium, tantalum, and iron). These reagents in 1.0 N HCl give white precipitates with zirconium. The sensitivity of the reaction with the first

reagent is 1:1,000,000, while for the second it is 1:1,500,000. The composition of the precipitates obtained approximates to the formulas $ZrO(C_6H_5SeO_2)_2$ and $ZrO(C_{10}H_7SeO_2)_2$. For quantitative determinations these precipitates are calcined and the zirconium is weighed as ZrO_2. These reagents permit determination of zirconium in steel and evdialite. The absolute experimental error for zirconium contents ranging from 2.0 to 10% does not exceed ± 0.01%.

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* Original Russian pagination. See C.B. Translation.

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AMPEROMETRIC TITRATION OF QUADRIVALENT URANIUM WITH AMMONIUM VANADATE

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The problem of the amperometric titration of uranium is one which has not been investigated enough. The discharge potentials of both quadrivalent and sexivalent uranium are known. The polarographic characteristics of the elements which can be used as oxidizing agents for the titration of quadrivalent uranium have been studied; a method has also been suggested for the amperometric titration of uranium with trivalent iron [1].

We used a solution of ammonium metavanadate as an oxidizing agent for the amperometric titration of quadrivalent uranium. Vanadium is reduced to the quadrivalent state on a dropping mercury electrode at a potential of about +0.1 volt.

The visual method for the vanadometric titration of quadrivalent uranium with phenylanthranilic acid, which was suggested by Syrokomskii [2] and which we have also studied, is very sensitive but its application is limited by the limits of the acidity of the solutions to be titrated of 5 N to 13.5 N with respect to sulfuric acid. When the acidity of the solution is less than 4 N and greater than 13.5 N, phenylanthranilic acid is unstable: in the first instance the color change is later, while in the second instance the color change is earlier than the equivalence point. Further, the visual method is not suitable for titration of colored solutions.

First of all, we took current – voltage curves for ammonium vanadate in the following media: 1 N H_2SO_4, 1 N HCl and 1 N $HClO_4$. It is clear from Fig. 1 that the limiting current for vanadium is clearly defined in all the acids indicated. By using these acids, it is possible to carry out amperometric determination of uranium in the potential range 0 to -0.16 volt.

TABLE 1

Potential 0 volt				Potential 0.1 volt			
U taken, in mg	V, ml NH_4NO_3 solution	U found, in mg	Error, in %	U, taken, in mg	V, ml NH_4NO_3 solution	U found, in mg	Error, in %
0.220	0.32	0.220	0	0.220	0.31	0.217	1.4
0.280	0.40	0.276	1.4	0.280	0.39	0.280	0

Titration of quadrivalent uranium was carried out at zero potential in sulfuric acid solution by means of 0.006 N ammonium vanadate. Hydrogen was passed through the system for 30 minutes prior to carrying out titration, in order to remove oxygen which interferes with titration. As an example we have given in Fig. 1 the curve obtained for 0.22 mg uranium (Fig. 2). Several determinations of uranium were carried out by means of the method described above at potentials of 0 and –0.1 volt.

It follows from the results given in Table 1 that amperometric titration of quadrivalent uranium by means of ammonium vanadate can be carried out with satisfactory accuracy, both at 0 volt, and at –0.1 volt.

In the following series of tests, uranium was titrated wi[redacted]onium vanadate in various acids. Changes n the acidity of the solution within the limits 0.1 N to 1 N, f[redacted]ic, hydrochloric, and perchloric acids have almost no effect on the titration results (Table 2).

[redacted]anium can be titrated with reasonable accura[redacted]means of 0.005 N ammonium metavanadate a[redacted]s the uranium concentration does not excee[redacted]/ml; the mean relative error is 1-3%.

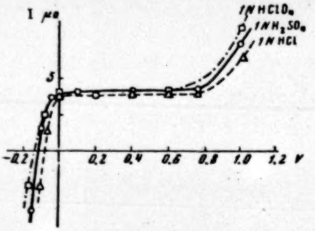

Fig. 1. Current – voltage curves for vanadium (5) in 1 N solutions of H_2SO_4, HCl, and $HClO_4$; ○ – 1 N H_2SO_4; △ – 1 N HCl; □ – 1 N $HClO_4$.

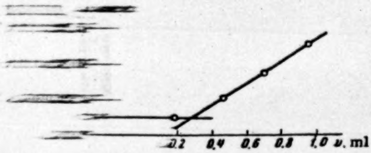

Fig. 2[redacted]rometric titration of quadrivalent urani[redacted]0.006 N ammonium vanadate solution.

Further dilution of the ammonium vanadate solution affects t[redacted]e of the curve considerably: the curve becomes flatter so that the error in determining the equivale[redacted]t increases.

The presence of the electrolytes: KCl, K_2SO_4, and NH_4[redacted]a solution with the same acidity in each case, namely H_2SO_4 (0.1 N), had no effect on the results of a[redacted]etric titration of uranium.

TABLE 2

(0.185 mg of U taken)

Acid	U found, in mg	Difference, in mg	Error, in %
0.1 *N* H_2SO_4	0.189	+0.004	2.2
1.0 *N* H_2SO_4	0.184	–0.001	0.6
0.1 *N* HCl	0.184	–0.001	0.6
1.0 *N* HCl	0.191	+0.006	3.2
0.1 *N* $HClO_4$	0.183	–0.002	1.1
1.0 *N* $HClO_4$	0.189	+0.004	2.2

T[redacted]3

U[redacted] in[redacted]	[redacted]ectrolyte con[redacted]nt, in g	U found, in mg	Difference, in mg
0.[redacted]	0.2 KCl	0.076	–0.001
0.[redacted]	2.0 KCl	0.092	–0.002
0.[redacted]	0.4 K_2SO_4	0.063	0
0.[redacted]	4.0 K_2SO_4	0.062	–0.001
0.[redacted]	1.3 NH_4Cl	0.061	–0.002

In view of the fact that iron is the element which acc[redacted]s uranium most often, it was of interest to find a method for determining uranium amperometrically [redacted] separating uranium from iron. In order to solve this problem, an attempt was made to complex iro[redacted]able complex ion.

A very good complexing agent for divalent iron is otho[redacted]throline ($C_{12}H_8N_2$), which complexes Fe^{2+} as a stable complex with a bright red color. Quinqueva[redacted]anadium does not oxidize this complex compound. At the same time quadrivalent uranium does no[redacted] complex with orthophenanthroline, and in the presence of the latter, uranium can be titrated comple[redacted]h vanadate. In order to carry out determinations, the solution containing uranyl sulfate and iron su[redacted]Fe = 1 : 25) was reduced with a liquid zinc amalgam in a hydrochloric acid solution, excess (10 m[redacted]phenanthroline was then added; the solution thereupon acquired a bright red color; the volume of the sol[redacted]s 25 ml while the H_2SO_4 concentration was 0.1 N. The results obtained are given in Table 4.

The mean error for the amperometric titration of ura[redacted]the presence of iron complexed with orthophenanthroline amounts to 3-6%.

TABLE 4

U taken, in mg	U found in mg, in the presence of orthophenanthroline	U found, in mg, in presence of iron and orthophenanthroline	Difference in mg
0.091	0.090	0.093	+0.002
0.091	0.091	0.095	+0.004
0.120	—	0.122	+0.002
0.120	—	0.125	+0.005

TABLE 5

U taken, in mg	Complexon III, in mg	U found, in mg	Difference, in mg
0.258	25	0.259	+0.001
0.258	50	0.256	−0.002
0.162	100	0.168	+0.006
0.258	100	0.259	+0.001

TABLE 6

U taken, in mg	Element added		U found, mg	Error, in %
0.130	Cr	Weight ratio of M: U = 25 : 1	0.135	3.9
0.190	Ni		0.196	3.1
0.162	Bi		0.156	3.7
0.192	Pb		0.189	1.6

For preventing possible hydrolysis, or formation of sparingly soluble sulfates, it is expedient to add Complexon III to the solution to complex lead, bismuth, chromium, and nickel. Addition of Complexon III does not affect the results of amperometric titration of uranium (Table 5).

Results of determinations of uranium in the presence of chromium, nickel, bismuth, and lead are given in Table 6.

SUMMARY

The possibility has been demonstrated of carrying out an amperometric titration of quadrivalent uranium (down to 2.5 γ/ml) by means of ammonium vanadate with an accuracy of 1-3%. Interference on the part of iron can be eliminated by addition of orthophenanthroline, while interference from chromium, nickel, lead, and bismuth can be eliminated by addition of Complexon III.

The mean error for uranium determination is 3-4%.

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CHROMATOGRAPHIC SEPARATION OF COBALT AND NICKEL DURING ANALYSIS OF ORES AND ALLOYS

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During the analysis of ores and alloys, cobalt and nickel, whose physicochemical properties are similar, are separated from each other by a number of chemical techniques; these techniques include precipitation of cobalt by α-nitroso-β-naphthol according to Ilinskii [1], Chugaev's method of separating nickel [1], precipitation of cobalt by persulfate and lead peroxide from sulfate solutions, and many others [2]. In addition to precipitation methods, extraction [3-5 etc.] and electrolytic (in particular [6-8]) methods of separating these elements are also known.

Recently there have been indications that ion-exchange chromatography can be successfully used for this purpose; this technique has a number of advantages [9]; in particular, the anion-exchange method is being successfully developed. When metals are separated by the anion-exchange technique, the ones that are sorbed by the active groups of the resin are those that form complex anions.

Anion exchange frequently permits separation to be carried out in a shorter time than cation exchange. This cutting down of the time required for effecting separation is favored by the fact that desorption of complex anions sorbed by the anion-exchange resin from a medium containing a strong electrolyte, can be realized simply by changing the electrolyte concentration, or by using water.

In this connection. many different makes of anion-exchange resins have been synthesized recently. Several of them have found wide application, and have started to find use in analytical chemistry [10]. Of Russian anion-exchange resins, EDE-10 (a condensation product of ethylenediamine and epichlorohydrin) and AN-2F (the condensation product of polyethylenediamine, phenol, and formaldehyde) strongly recommend themselves. The most widely used foreign makes are the American resins Dowex-1, Dowex-2, and Amberlite IRA 400.

The problem which formed the subject of the work described here was to separate cobalt and nickel in a hydrochloric acid medium using EDE-10, and to develop a method which could be used for the analysis of ores and alloys. During a study of the sorption capacity of cobalt and nickel, results obtained previously on Dowex-1 were used [11]. It was found tha maximum absorption of cobalt occurs from 9 N HCl, in which it forms a fairly stable ion $[CoCl_4]^{2-}$, while nickel does not form appreciable concentrations of complex anions throughout the whole HCl concentration range (0.1–12 N).

The radioisotopes Co^{60} and Ni^{65} were used for studying the comparative sorption capacity of Dowex-1 and EDE-10. Their radiochemical purity was checked on the basis of their half-life periods and their maximum β-radiation energy. Columns 10 cm long and 5 mm in diameter were used. The particle size of the anion-exchange resins in the chloride form was about 50 mesh. Before loading the resin into the column it was washed with 9 N HCl; an active preparation of Co^{60} and Ni^{65} (20-30 thousand impulses/minute each) in 0.1-1 ml of concentrated HCl was then introduced onto the column. The column was eluted with 9 N HCl at the rate of 5-10 drops/minute. Nickel, which under these conditions does not form complex anions, passed into the filtrate. The filtrate was analyzed for nickel radiometrically; for this purpose 2 drops of filtrate was collected on a target; the solution was evaporated and the activity measured on a torsion counter. When all the nickel had been eluted from the column, a fact which was established by the disappearance of activity in the filtrate, the cobalt was eluted with 0.5 N HCl. Under these conditions, the anion $[CoCl_4]^{2-}$ breaks down, and passes into the filtrate in the form of its simple cation. This filtrate was also analyzed radiometrically. On the basis of these radiometric measurements, the elution curves for cobalt and nickel shown in Figs. 1 and 2 were constructed. These curves show that when the conditions outlined above are observed, complete separation of nickel and cobalt is achieved on both Dowex-1 and EDE-10. It is also evident that EDE-10 behaves like Dowex-1, although tailing is observed in the case of EDE-10; this tailing is probably the result of the fact that the EDE-10 resin was ground to give the requisite particle size, in contrast to Dowex-1 which is supplied in the form of small spheres; this grinding of the EDE-10 probably results in the formation of microcracks which slow down the elution process.

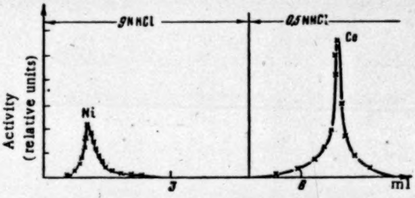

Fig. 1. Elution curves for Ni^{65} and Co^{60} on Dowex-1.

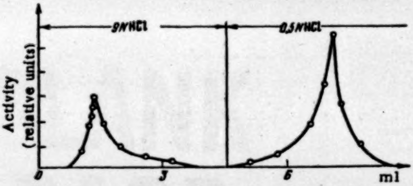

Fig. 2. Elution curves for Ni^{65} and Co^{60} on EDE-10.

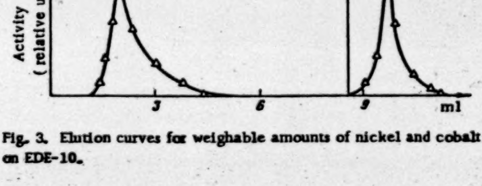

Fig. 3. Elution curves for weighable amounts of nickel and cobalt on EDE-10.

From the results of activity measurements carried out on the filtrates, the amount of cobalt and nickel separated from the columns was determined quantitatively by simply summing the activities. The results obtained by this summation showed that cobalt and nickel are quantitatively eluted from the resin; no losses or mixing is observed.

Weighable amounts of cobalt and nickel were then separated on the same column using the same experimental technique as that described above. The analysis of the individual filtrates was carried out by means of color reactions in this case; nickel was detected with dimethylglyoxime, while cobalt was detected with α-nitroso-β-naphthol. During the elution process, the points at which nickel and cobalt started and finished passing into the filtrate respectively were established; elution curves (Fig. 3) were also constructed on the basis of visual observation of the changes in color intensity for the color reactions, and on the basis of radiometric control with added Co^{60} and Ni^{63}.

TABLE 1

Taken, in mg		Found, in mg		Difference, in mg		Error, in %	
Ni	Co	Ni	Co	Ni	Co	Ni	Co
0.503	3.5	0.498	3.41	—0.005	—0.009	—0.99	—2.55
0.503	3.5	0.496	3.5	—0.007	0	—1.4	0
1.06	1.75	1.10	1.78	+0.04	+0.03	+3.7	+1.71
1.06	1.75	1.07	1.79	+0.01	+0.04	+0.99	+2.28

Quantitative determination of cobalt and nickel in the appropriate fractions of the filtrate was realized by well-known gravimetric and photometric methods. Nickel was determined by the Chugaev method, while cobalt was determined by the Ilinskii method.

It follows from the results given in Table 1 that during separation of weighable amounts of cobalt and nickel, these elements quantitatively and separately pass into the corresponding fractions of the filtrate.

Determination of Cobalt and Nickel during the Analysis of Ores and Alloys. We had at our disposal an arsenic-cobalt ore containing S, Fe, Si, Ni and other impurities, and alloys containing about 20 elements including Fe, Co, Ni, Cr as base elements.

The methods of separating nickel with dimethylglyoxime and cobalt with α-nitroso-β-naphthol, particularly from solutions containing large amounts of components, are not suitable and are unreliable. Accordingly, on the one hand we made use of the similarity in physicochemical properties of cobalt and nickel when they are in a cationic state, for separating them from mixtures of other ions, while on the other hand the large difference in the capacity of the two elements to form complexes in hydrochloric acid solutions was used for separating these elements from each other. For isolating cobalt and nickel from solutions of ores and alloys, rubeanic acid was used, since this reagent selectively precipitates cobalt and nickel when copper is absent [12]. When copper is present, however, it still need not interfere with the final determination of cobalt and nickel, since it can be readily removed from them on the column on account of the comparatively high stability of its chloride complex in dilute HCl. In such a case, the cobalt is eluted with 4 N HCl, while the copper is eluted with 2.5 N HCl after the complete elution of cobalt. In order to check on the completeness of the separation of the rubeanates of cobalt and nickel by the technique described below, a synthetic mixture of cobalt and nickel to which Co^{60} and Ni^{63} had been added, was used. At the same time, the behavior of iron during precipitation of the rubeanates was established by means of the radioisotope Fe^{59}, since iron was a basic component of the ores and alloys at our disposal.

TABLE 2

Taken in imp./min			Found in prec. of rubeanates, imp./min			Precipitation, in %		
Fe	Co	Ni	Fe	Co	Ni	Fe	Co	Ni
6160	9216	2600	61	9200	2508	0.9	100.0	97.1
6160	9216	2600	42	9101	2475	0.7	98.8	96.9

From the results given in Table 2, it is obvious that cobalt and nickel are completely precipitated by rubeanic acid, while iron — as the citrate complex — remains in the filtrate. Trapping of iron is reduced to a minimum by careful washing of the precipitate.

The ores were analyzed as follows. 500 mg of the ore was ignited in order to remove most of the sulfur and arsenic, after which the ore was dissolved in aqua regia. When decomposition was complete, the insoluble residue consisting of SiO_2 was filtered off. The residue was washed with dilute HCl and hot water. The filtrate plus washings were collected in a 25-ml standard flask and diluted to the mark with water. 2-4 ml aliquots of this solution were taken for analysis; to the aliquot was added 10% citric acid, after which the solution was neutralized with ammonia to a pH of about 8. 3-4 ml of a 0.5% solution of rubeanic acid was added to this solution. The precipitate obtained was left to stand for 3-4 hours, after which it was filtered through a No. 4 glass filter; it was washed 5-6 times with 1% NH_4Cl, and finally dissolved in aqua regia. The solution obtained, with a volume of 5-6 ml, was evaporated to dryness and the dry residue dissolved in the minimum volume of 9 N HCl. The subsequent analytical procedure adopted was that described above: the hydrochloric acid solution of cobalt and nickel was passed through a column of EDE-10 resin, after which the cobalt and nickel contents of the appropriate fractions of filtrate were determined by the usual analytical methods. The results obtained are given in Table 3.

TABLE 3

Sample	Sample weight, in mg	Found, in mg		Content in ore and alloys, %	
		Ni	Co	Ni	Co
Ore	20	0.3	4.249	1.51	20.1
	20	0.29	4.250	1.49	20.03
	40	0.59	8.55	1.50	20.20
Alloy*	40	5.054	4.18	12.62	10.42
	40	5.03	4.3	12.6	10.78

*Standard sample with a content of Ni — 12.7%, Co — 10.38%.

The alloy was analyzed as follows. 1 g of alloy was dissolved in aqua regia. When solution was complete, an aliquot of the solution was evaporated to dryness and the dry residue dissolved in HCl (sp.gr. 1.09) to which citric acid was added. The insoluble residue was filtered off and washed with dilute HCl, after which the filtrate plus washings were transferred to a 50-ml standard flask, and the volume made up to the mark with water. This solution was used for determining the nickel and cobalt content as described above.

It follows from the results given in Table 3 that the method of determining cobalt and nickel by means of an anion-exchange resin gives reasonably accurate results.

SUMMARY

Separation of weighable amounts of cobalt and nickel on an anion-exchange resin has been achieved by using conditions established beforehand by means of Co^{60} and Ni^{65}; the resin used was EDE-10. The method developed has been used for separating cobalt and nickel during analysis of ores and alloys.

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NEW METHODS FOR THE QUANTITATIVE DETERMINATION OF NITROGEN, SULFUR, AND HALOGENS ON ONE ALIQUOT OF ORGANIC MATERIAL

COMMUNICATION 4. THE USE OF CALCIUM FOR DECOMPOSING TEST MATERIAL*

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In previous articles we have shown that nitrogen, sulfur, and halogens can be quantitatively determined in organic materials by means of powdered magnesium metal [1]. One of the drawbacks of the method is the necessity of treating the reaction mixture with acid, and this leads to the formation of an explosive mixture of silicon hydrides, hydrogen, and air; accordingly, the decomposition has to be carried out in an inert gas atmosphere. In order to simplify the magnesium method and to eleminate the drawbacks indicated, we decided to use powdered calcium instead of magnesium for determining nitrogen, sulfur, and halogens in organic materials.

Calcium, even at normal temperatures, reacts with water and readily combines with oxygen, nitrogen, sulfur, and halogens. The capacity of calcium, on heating, to combine with traces of air and other gaseous materials is used technically for creating a vacuum. Calcium in contrast to magnesium does not react with glass at 700-750°. The melting point of calcium is 850° while the boiling point is 1487°. Magnesium melts at 650° and boils at 1100°.

The method consists, in principle, of heating the test organic material containing nitrogen, sulfur, and halogens with powdered calcium at 700-750° in an atmosphere of ether vapor or hydrogen. Under these conditions calcium nitride, sulfide, and halides are formed and nitrogen, sulfur, and halogens are determined in these.

Determination of Nitrogen. The material was decomposed in the apparatus shown in Fig. 1.

The test material (0.0300-0.0600 g) was placed on the bottom of the glass tube 1 by means of a fine metal spatula.** The aliquot was mixed with 20-30 mg of powdered calcium,*** and the mixture covered with a further 1-1.5 g of calcium. The layer of calcium in the tube should occupy 100-120 mm length of the tube. The air was displaced from the tube by pouring 1 ml of ether into it.

A rubber tube 2 connected to the tubes 3 and 4 was fitted onto the open end of the tube. A bunsen valve was fitted onto tube 3, and introduced under a cylinder containing water. The air in tubes 2,3 and 4 was also expelled by pouring 1.5 ml of ether into them. When tube 1 had been prepared for analysis, it was placed in a tubular open electric oven heated to 700-800°, or was heated with gas burners. First the layer of calcium furthest removed from the aliquot was heated; the heating zone was then gradually extended toward the aliquot. The heated calcium combined with all the gaseous products formed during the decomposition of the test material. This could be observed by sucking in of water and flattening of tube 1. In order to prevent water getting into the tube used for the analysis, tube 2 was fitted with a screw clip at the point where it was connected to tube 1. The screw clip was tightened up when the water being sucked into the apparatus appeared in the connecting glass tube 4.

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*Communication 3, J. Anal. Chem. 11, 233 (1956) (see C.B. Translation).

**The spatula was a fine copper wire 300 mm long, diameter 3 mm; one end was flattened to form a small blade suitable for introducing the test material into the tube.

***Calcium should not be kept in contact with air for any length of time; it is best stored in glass bottles with ground glass stoppers, the bottles being filled with carbon dioxide.

When all the calcium layer had been heated to the temperatures indicated above (15-20 minutes) the electric oven was switched off. A vacuum should still be maintained in the cooled analytical tube (a point which could be verified by the fact that the rubber tube 2 was still flattened) otherwise the result for nitrogen would be too high. Decomposition of organic material by heating with calcium can also be carried out with another variant of the apparatus; this apparatus which is shown in Fig. 2 permits one to omit the stage of expelling the air by means of ether or hydrogen.

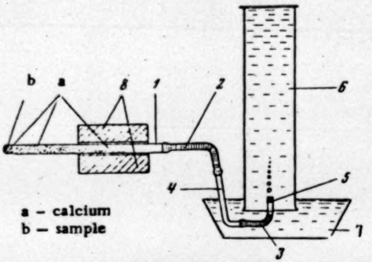

Fig. 1. Apparatus for decomposition of organic material: 1) glass tube 250 mm long with an internal diameter of 5-6 mm, fused at one end; 2 and 3) rubber tubing 200 mm long, 4-5 mm diameter; 4) glass tube; 5) Bunsen valve; 6) cylinder containing water; 7) crystallizing basin.

Tube 1 was prepared for analysis as described above and the aliquot of test material and powdered calcium introduced into it. In order to remove air from tube 1, 200-300 mg of powdered calcium was placed in quartz tube 3, and tubes 1 and 3 connected to each other by a piece of vacuum rubber tubing 2.

The calcium in tube 3 was heated first to 800°. The heated calcium in the course of 20 minutes combined with all the air in the apparatus. Tube 1 and its contents of test material was then heated as described above. When the tube had cooled it was withdrawn from the oven and cut open; the part of the tube not containing calcium was rejected, while the part of the tube containing test material and calcium was wrapped up in filter paper; the tube was then broken up in the filter paper by a few blows from a hammer and the whole transferred to a dry round-bottom flask for distilling off the ammonia. 20 ml of 0.05 N mineral acid and 2 drops of indicator (methyl red) were placed in the receiver. 80-100 ml of distilled water was introduced into the flask by means of a dropping funnel in order to decompose the reaction mass.* Since calcium reacts vigorously with water, the latter was added dropwise initially. When the reaction had ceased the rest of the water was added. The flask was heated and the ammonia distilled over into the receiver (20-25 minutes). Excess acid in the receiver was titrated with 0.05 N alkali.

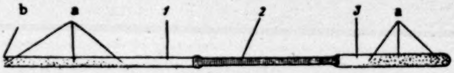

Fig. 2. Simplified decomposition apparatus: 1) glass tube (described in the text); 2) rubber vacuum tubing 50-60 mm long; 3) quartz or porcelain tube 150 mm long, 6-7 mm in diameter fused at one end; a) calcium; b) test material.

The results of some of these determinations are given in the Table.

Determination of Sulfur. Test material was decomposed in the apparatus shown in Fig. 1, the method used for determining nitrogen being followed. An aliquot of test material was introduced into tube 1 and covered with 1-1.5 g of powdered calcium (see determination of nitrogen *).

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*Decomposition can also be effected with 30% ethanol. In this case the reaction is not quite so turbulent.

Tube 1 was prepared for analysis and the apparatus assembled (Fig. 1).

Tube 1 was placed in the tubular open electric oven and heated as described for nitrogen determination. When heating was finished, the electric oven was switched off and the cooled tube withdrawn; the latter was then wrapped up in filter paper and broken up; the broken mixture of glass, paper and residue from decomposition were then transferred to a dry round-bottom distillation flask in order to drive off the hydrogen sulfide. Three absorption flasks were used for absorbing the hydrogen sulfide. The first of these contained 25-30 ml of a mixture of a 10% solution of sodium acetate and 10% zinc sulfate acidified with a few drops of concentrated acetic acid. The second and third flasks contained 20 and 10 ml respectively of the same mixture. A small excess of 4% sulfuric or hydrochloric acid was then added slowly – particularly to start with – to the distillation flask until the calcium had dissolved completely and the calcium sulfide had decomposed. When all the acid had been added the flask was heated and the hydrogen sulfide driven over with the hydrogen liberated. Distillation was stopped when one third of the contents of the flask had been distilled. The hydrogen sulfide was mainly absorbed as zinc sulfide in the first receiver.

When distillation was complete, the contents of all three receivers were poured together and 20 ml of 0.05 N iodine solution acidified with a few drops of 10% hydrochloric acid added; after standing for three minutes excess iodine was titrated with sodium thiosulfate. Results of some of these determinations are given in the Table.

Halogen Determination. The analysis was carried out in the apparatus shown in Fig. 1. The aliquot of test material and 1-1.5 g of powdered calcium were introduced into the tube 1 as described above (see determination of nitrogen) but, in contrast to the nitrogen determination, there was no need to expel the air from the flask.

Tube 1 was heated in the electric oven or with gas burners as described above. When heating had been completed, the cold tube was wrapped up in filter paper, the whole broken up with a hammer, and all the pieces transferred to a dry 0.5-liter tall beaker. The contents of the beaker were treated with 10-70 ml of 5% nitric acid, which was initially added dropwise in order to prevent sputtering of the solution. Acid was added until all the calcium had dissolved. The solid residue (carbon, glass) was filtered off and the filter plus solid residue washed carefully with distilled water. 20 ml of 0.05 N silver nitrate was added to the filtrate, and the solution titrated with 0.05 N ammonium thiocyanate in the presence of 0.5 ml of a saturated solution of ferric alum.**

Results of some determinations carried out in this way are given in the Table.

Determination of Sulfur and Nitrogen in Organic Materials on One Aliquot of Test Material. The aliquot of test material plus 1-1.5 g of calcium was placed in glass tube 1 of the apparatus shown in Figs. 1 and 2 (see nitrogen determination). The air was removed from the tube either by means of ether or by heating with calcium as described in the nitrogen determination.

Tube 1 prepared for analysis as described was then heated by the technique given above. When heating was finished, the tube was wrapped up in a filter paper, the whole broken up, and all the pieces transferred to the flask of the apparatus used for removing hydrogen sulfide (see sulfur determination). The reaction mass was decomposed with 80-100 ml of 4% sulfuric or hydrochloric acid, the hydrogen sulfide was distilled over and the sulfur content determined iodometrically (see sulfur determination). When the hydrogen sulfide had been determined, the condenser and the Kjeldhal setup was washed with distilled water, and the receivers for absorbing hydrogen sulfide replaced by a receiver for the ammonia (see nitrogen determination). The residue in the distillation flask was made alkaline with 50% alkali and, having distilled over the ammonia, the nitrogen determined.

Results of some of these determinations are given in the Table.

Determination of Nitrogen and Halogens on One Aliquot. Filling of the tube, expulsion of air from the

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* When sulfur is determined there is no need to expel the air.

** Since commercial calcium metal always contains some chloride, it is essential to carry out a blank and correct for this chloride.

TABLE

Test material	Calc. N, %	Found N, %	Difference, %	Calc. S, %	Found, S, %	Difference, %	% Halogen		
							calc.	found	difference
Para-aminobenzoic acid $C_7H_7O_2N$	10.21	10.13	−0.08						
Azobenzene $C_{12}H_{10}N_2$	15.37	15.36	−0.01						
α-Naphthylamine $C_{10}H_9N$	9.78	9.80	+0.02						
Diphenylamine $C_{12}H_{11}N$	8.27	8.29	+0.02						
Nitrocinnamic acid $C_9H_7O_4N$	7.25	7.01	−0.24						
Dimethylaminobenzene $C_{14}H_{15}N_3$	18.66	18.68	+0.02						
Acridine $C_{13}H_9N$	7.81	7.68	−0.13						
Sulfosalicylic acid $C_7H_{10}O_8S$				12.61	12.51	−0.10			
Meta-xylyltaurine $C_{10}H_{15}O_3NS$				13.98	13.81	−0.17			
Sodium 3-methyl-5-(α-furyl)-pyrazoline-1-dithiocarbonate $C_9H_9ON_2S_2Na$				25.82	25.78	−0.04			
Hexachloroethane C_2Cl_6							89.89	89.87	−0.02
Dibromobenzene $C_6H_4Br_2$							67.70	67.53	−0.17
1-Phenyl-3-carbethoxy-4-chloro-5-hydroxybenzofuran $C_{17}H_{13}O_4Cl$							11.19	11.23	+0.04
1-Phenyl-3-carbethoxy-7-chloro-5-hydroxybenzofuran $C_{17}H_{13}O_4Cl$							11.19	10.94	−0.25
1-Chloro-2,3-dimethyl-4-phenylbutene-2 $C_{12}H_{15}Cl$							18.21	18.34	+0.13
1-Chloro-4-(para-chlorophenyl)-butene-2 $C_{10}H_{10}Cl_2$							35.26	35.07	−0.19
Para-toluenesulfamide $C_7H_9O_2NS$	8.18	8.01	−0.17	18.72	18.56	−0.16			
Diphenylthiourea $C_{13}H_{12}N_2S$	12.27	12.08	−0.19	14.04	13.83	−0.21			
Mercaptobenzthiazole C_7H_5NS	8.35	8.26	−0.09	38.31	38.08	−0.23			
3,5-Diphenylpyrazoline-1-thiocarbanilide $C_{22}H_{19}N_3S$	11.76	11.49	−0.27	9.00	9.03	+0.03			
S-(β-cyanethyl)-5-(α-furan)-3-methylpyrazoline-1-dithiocarbonic acid $C_{12}H_{13}ON_3S_2$	15.04	15.32	−0.28	22.95	23.00	+0.05			
3-Methyl-5,5-pentamethylenepyrazoline-1-thiocarbanilide $C_{16}H_{21}N_3S$	14.62	14.44	+0.18	11.15	10.83	−0.32			
1,3-Dimethyl-5-(1-amino-2-sulfo) ethylbenzene $C_{10}H_{15}O_3NS$	6.11	6.36	+0.25	13.98	14.08	+0.10			
1-Phenyl-2-methyl-3-acetyl-5-(para-bromobenzoxy)-indole $C_{24}H_{18}O_3NBr$	3.12	3.14	+0.02				17.82	17.87	+0.05
1-Ethyl-2-methyl-3-carbethoxy-4,7-dichloro-5-methoxyindole $C_{15}H_{17}O_3NCl_2$	4.24	4.40	+0.16				21.47	21.19	−0.28
Chloraniline C_6H_6NCl									
Sulfosalicylic acid $C_7H_{10}O_8S$	5.75	5.63	−0.12	6.01	5.83	−0.18	14.55	14.79	+0.24

apparatus, and heating of tube 1 were carried out according to the technique described already (see nitrogen and halogen determinations).

The reaction mass was transferred to the flask for distilling off the ammonia, where it was decomposed with water, the ammonia driven over and the nitrogen content determined (see nitrogen determination). When the ammonia had been driven off, the residue in the distillation flask was acidified with 5% nitric acid until the calcium hydroxide had dissolved completely; the solution was then filtered free of residual carbon and glass and the residue on the filter washed with distilled water; the halogen content of filtrate plus washings was then determined (see halogen determination).

Results of some of these determinations are given in the Table.

Determination of Sulfur and Halogens on One Aliquot. Analysis was carried out in the apparatus shown in Fig. 1. The reaction mass was transferred to a flask for driving off the hydrogen sulfide; there it was broken down with acid (see sulfur determination) and, having distilled over the hydrogen sulfide, the sulfur content determined iodometrically. The residue remaining after distilling off the hydrogen sulfide was filtered free of particles of carbon and glass. These particles were carefully washed on the filter with distilled water and the halogen content determined by the Volhard method as described already (see Halogen determination).

Results of some of these determinations are given in the Table.

Quantitative Determination of Nitrogen, Sulfur, and Halogens on One Aliquot of Organic Test Material. Decomposition of the organic material was carried out in the apparatus shown in Figs. 1 and 2. Introduction of test sample, filling the tube, and removing the air were carried out by the method described for nitrogen determination. When heating had been finished the cooled tube was broken up in a filter paper, and the pieces transferred to the flask of the apparatus used for distilling over the hydrogen sulfide; the reaction mass was decomposed in this flask with acid, and the hydrogen sulfide liberated distilled over into the receivers; the sulfur content of the original organic test material was then determined iodometrically, (see sulfur determination). In order to determine nitrogen the receivers used for absorbing hydrogen sulfide were replaced by a receiver for collecting ammonia (see simultaneous determination of sulfur and nitrogen). The acid solution in the distillation flask was made alkaline and the ammonia distilled over; the nitrogen content was then determined.

When both sulfur and nitrogen had been removed, the contents of the flask were acidified with nitric acid until all the calcium hydroxide had dissolved. Solid residues were filtered off, and washed on the filter with distilled water; the halogens were then determined argentometrically in the combined filtrate plus washings (see halogen determination).

Some results of determinations carried out in this way are given in the Table.

SUMMARY

A method is described for the quantitative determination of nitrogen, sulfur, and halogens in organic materials, in which the latter are heated with powdered calcium.

This method permits quantitative determination of the elements indicated either singly, in twos, or threes on one aliquot of test material. The use of calcium speeds up and simplifies analysis, and prevents formation of explosive mixtures.

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* Original Russian pagination. See C.B. Translation.

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A MICRO METHOD FOR THE DETERMINATION OF HALOGENS IN ORGANIC MATERIALS.

COMMUNICATION II.* DETERMINATION OF HALOGENS BY COMBUSTION IN A STREAM OF OXYGEN

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During determination of halogens in organic compounds it is essential to mineralize the halogens quantitatively, converting them thereby into the ionic state by oxidation or reduction. Of the reduction methods, we have studied that of Korshun and Chumachenko [1] – fusion of the organic material with potassium metal – while of the oxidation methods – the Pregl method [2] – we have tried breaking down the organic material by combustion in a stream of oxygen, and subsequently passing the gases over heated platinum and isolation of the combustion products of the halogen. Combustion was carried out in a quartz beaker. The liquid used for absorbing chlorine and bromine was a saturated solution of sodium carbonate to which a few drops of a saturated solution of hydrazine sulfate was added (instead of bisulfite), while for iodine the solution used for absorbing it was a 5% solution of sodium hydroxide. Chlorine was determined gravimetrically while iodine was determined volumetrically by the Leipert method [3] – titration with sodium thiosulfate. Analysis was carried out in apparatus made in the Klinsk Glass Factory "Laborpribor."

Because of defects in the apparatus the results obtained were low. The absorption apparatus connected via ground joints to the quartz tube was not made of heat-resisting glass.

During analysis of iodine-containing materials at an oxygen throughput of 4-8 ml per minute, some of the iodine was held back on the cold parts of the combustion tube and on the joints of the absorption apparatus. When the tube near the joints was heated in order to drive over all the iodine into the absorption apparatus, the joints cracked. The use of spirals in the absorption apparatus did not guarantee complete absorption of the gas by the absorption liquid, so that the results for chlorine and bromine were also low. Accordingly, in order to get better results, we used an apparatus similar to that recommended by Korshun and Sheveleva [4] for the simultaneous determination of carbon, hydrogen, and sulfur by a gravimetric method (Fig. 1).

The absorption apparatus which was connected to the combustion tube through ground joints was made from quartz; this made it possible to heat the tube near the joint and also heat the joint itself, and prevent deposition of iodine on the tube walls. In order to improve absorption efficiency, the absorption apparatus was half-filled with fine glass rings or beads. The combustion tube finished in a capillary nozzle, which passed into the absorption apparatus, and favored quantitative transfer of the gases into the absorption liquid.

In order to prevent possible breakthrough of gas, a test tube with a fused-in Schott disc was connected to the nozzle of the quartz absorption apparatus through a side capillary side tube, a piece of rubber tubing being used for connecting the capillary to the absorption apparatus. A hydraulic liquid seal of absorption liquid was set up in the test tube; part of the liquid being on the disc. The oxygen throughput was assessed by connecting the test tube to a Mariott bottle.

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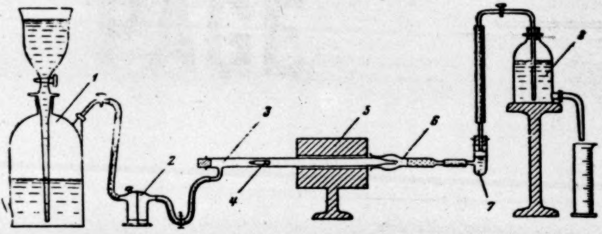
The results obtained on this setup, as can be seen from Table 1 are very close to the theoretical values.

TABLE 1

Test compound	Sample wt., mg	Halogen found, %	Halogen calc.,%	Difference, %
Meta-iodobenzoic acid	3.210	51.05	51.39	—0.34
I-C_6H_4COOH	3.005	51.08		—0.31
β-Iodopropionic acid	4.580	63.39	63.46	—0.07
I-CH_2CH_2COOH	3.205	63.21		—0.25
Tetrachlorophthalic acid	4.435	46.85	46.70	+0.18
$C_6Cl_4(COOH)_2$	3.410	46.76		+0.16
α,α,2,3,4-pentachlorotoluene	5.510	67.03	67.10	—0.07
$C_6H_2Cl_3CHCl_2$	3.960	66.85		—0.25
α,α,α,2,3,4-hexachlorotoluene	3.100	71.27	71.24	+0.03
$C_6H_2Cl_3CCl_3$	4.350	71.37		+0.13

The Pregl method which is difficult and takes rather a long time, requires a platinum catalyst; chlorine and bromine are given a gravimetric finish. We were attracted by the simple and rapid macro-method of determining halogens proposed by Fedoseev and Sobko [5]. Combustion in this case again was carried out in a stream of oxygen, but the oxygen throughput was considerably greater, and no catalyst was used.

Potassium iodide was used as the absorption medium. The chlorine and bromine liberated during combustion of the organic material displaced a corresponding amount of iodine; iodine was trapped by potassium iodide. Sodium thiosulfate was used for titration. The apparatus described above was also used for this method of determining halogens.



1) Gasometer containing oxygen; 2) Tishchenko flask; 3) quartz tube, 8-9 mm inner diameter, 350-400 mm long; 4) quartz beaker containing test sample; 5) open electric oven 140 mm long, temperature 800-850°; 6) quartz absorption apparatus, connected via a ground joint to the combustion tube; 7) supplementary absorption apparatus with a side tube and porous disc; 8) Mariott flask.

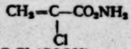
Experimental Technique. 3-7 mg of test material was placed in a quartz tube, or in a quartz or platinum boat, and subjected to thermal decomposition by means of a gas burner or an electric oven at a temperature 950-1000°. The gaseous decomposition products mixed with the oxygen, the throughput of which was 20-25 ml/minute, and passed through a tube heated by an electric oven to 800-850°. The liberated halogen was trapped in the absorption apparatus by means of potassium iodide. The tube or boat containing the aliquot was placed at a distance of 40-50 mm from the oven. The aliquot was heated for 12-15 minutes; the amount of oxygen used during this period was 300 ml. The oven was then moved off, the gases driven out and the system allowed to cool for 8-10 minutes while another 200 ml of oxygen was used. The total amount of oxygen used was 500 ml.

During the analysis of high molecular weight materials, a larger volume of oxygen was used, amounting to 700-800 ml. Before commencing an analysis 1.0-1.5 ml of a 10% solution of potassium iodide was introduced into the quartz absorption apparatus which was connected to the test tube with the side tube; this solution of potassium iodide was carefully swirled round to moisten the glass rings or beads. Crystalline potassium iodide (0.5-0.7 g) was carefully strewn onto the porous disc and over the rings in the quartz apparatus by means of a funnel, without taking off the ground joint; the absorption apparatus was then connected to the combustion tube while the oxygen stream was kept on. When the tube or boat plus test sample had been introduced into the apparatus, heating was commenced, the burner being gradually brought closer to the neck of the tube or boat containing the sample, and the sample carefully ignited; it was finally completely burnt. When the substance had been completely burnt, the tube was heated along all its length up to the point where it joined the electric oven which was fitted right up to the joint of the absorption apparatus.

When the system was cooled the contents of the absorption apparatus was washed out with a few portions of distilled water into a conical flask; three washings were enough (7, 9, and 11 ml).

According to the observations of P. N. Fedoseev and M. Ia. Sobko, during combustion of chlorine-containing compounds, free chlorine and hydrogen chloride are formed. Accordingly, for determining the latter in the presence of chlorine, 9 ml of 0.02 N potassium iodate or potassium biiodate was added. In the latter case, it was essential to carry out a blank in order to take account of the free iodine liberated by potassium biiodate.* For bromine and iodine determinations, addition of potassium iodate or biiodate was not necessary, since during combustion of organic compounds containing bromine and iodine, only the free halogen is liberated. The amount of iodine was determined by titration with sodium thiosulfate.

TABLE 2

Test material	Sample wt.,mg	Halogen found, %	Halogen calc., %	Difference, %
Poly para chloromethylstyrene $(C_8H_7CH_2Cl)_n$	3.360	23.50	23.30	+0.20
	3.650	23.43		+0.13
Sample IVS No. 8 $C_8H_{11}O_2Cl$	3.625	23.79	23.55	+0.42
	5.175	23.50		−0.05
Para-chloroaniline $C_6H_4ClNH_2$	3.325	28.28	27.95	+0.33
	3.375	28.31		+0.36
α-Chloroacrylic acid amide  $CH_2{=}\underset{\displaystyle Cl}{\underset{\vert}{C}}{-}CO_2NH_2$	3.610	33.96	33.60	+0.36
				+0.20
	4.090	33.80	33.60	−0.05
Tetrachlorophthalic acid $C_6Cl_4(COOH)_2$	4.185	46.65		+0.13
	3.345	46.83	46.70	+0.17
2, 4, 5-Trichlorotoluene $C_6H_2Cl_3(CH_3)$	4.850	54.64		−0.19
	3.100	54.28	54.47	−0.31
Polychlorovinyl $(-CH_2-CHCl-)_x$	3.115	56.42		−0.50
	3.305	56.23	56.73	−0.10
α, α, 2, 4, 5-Pentachlorotoluene $C_6H_2Cl_3\cdot CHCl_2$	5.030	67.00	67.10	−0.49
	5.995	66.61		−0.58
Hexachloroethane C_2Cl_6	4.390	89.27	89.85	+0.11
Sample IVS No. 4 $C_8H_{15}Br$	6.830	41.95	41.84	+0.18
	3.390	42.02		+0.05
5, 7-Dibromo-8-hydroxyquinoline $Br_2C_9H_4(OH)N$	3.330	52.80	52.75	+0.09
	3.715	52.84		−0.01
Para-dibromobenzene $C_6H_4Br_2$	4.750	67.87	67.88	−0.18
	4.800	67.70		−0.05
	5.380	67.83		+0.19
Iodoalkylate of 1-methyl-2-(para-tolyl)-	3.790	35.04	34.85	+0.18
benzimidazole $C_{16}H_{17}IN_2$	4.410	35.03		−0.10
	3.860	51.29	51.39	0.23
Meta-iodobenzoic acid $I-C_6H_4-COOH$	3.700	51.16		+0.02
	3.620	51.41	63.46	+0.09
β-Iodopropionic acid $I-CH_2-CH_2-COOH$	4.350	63.55	63.46	+0.04
	3.280	63.50		

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*Both potassium iodate and potassium biiodate can be used.

Before starting any analysis, 500 ml of oxygen was passed through the apparatus while the oven was switched on.

The analytical results are given in Table 2.

We successfully analyzed various halogenated polymers and copolymers, which are very difficult to analyze by combustion. Usually these compound only contain hydrogen, carbon, and oxygen in addition to the halogen. Analysis including sampling and titrating takes 35-40 minutes.

It should be pointed out that the micro method described above is not suitable for all organic materials. When the organic compound contains nitrogen as well as halogen, it is essential to know in what form it is present. Nitrogen present as amine, imine, or amide nitrogen or present in an aromatic nucleus does not interfere with halogen determination (Table 2). During pyrolysis of organic material in a quartz tube or boat, as Korshun and Limov observed [6, 7], nitrogen present in the forms indicated above is liberated in the elemental form. In nitro compounds part of the nitrogen is liberated as nitrogen oxides, and the results obtained will be high. In the same way it is impossible to analyze compounds containing sulfur as well as halogens; such compounds include free sulfonic acids and halosulfones.

The micro method developed was used for the determination of fluorine in organofluorine compounds. Analysis was carried out in the same apparatus. In contrast to the determination of the other halogens, the temperature of the oven was elevated to 950-1000° while a platinum contact was placed in the oven, or combustion was carried out in a platinum boat. During combustion the ground joint of the absorption apparatus was placed in the electric oven. Distilled water was used for absorbing the decomposition products.

When combustion was complete, the contents of the absorption apparatus was washed out into a conical flask. To this flask was added 0.5-0.7 g of crystalline potassium iodide and 9 ml of 0.02 N potassium iodate. The iodine liberated in an amount equivalent to the fluorine contained in the sample was titrated after 10 minutes with 0.02 N sodium thiosulfate.

TABLE 3

Test sample	Sample wt., mg	Halogen found in %	Halogen calc. in %	Difference, in %
Sample IVS No. 1	3.330	10.49	10.50	—0.01
	3.280	10.53		+0.03
Sample IVS No. 28	4.340	10.64	10.67	—0.03
	5.310	10.36		—0.31
Dimethylfluorostyrene $C_{10}H_{11}F$	3.190	12.61	12.66	+0.05
	3.550	12.62		+0.04
Methylfluorostyrene C_9H_9F	3.300	13.85	13.97	—0.12
	3.640	13.95		—0.02
	3.600	13.88		—0.09
Fluorobenzene C_6H_5F	3.400	19.87		+0.10
	3.380	19.77	19.77	0
	4.020	19.55		—0.22
1, 5-Hexafluoro-2-methyl-2-ol-pentanone-4 $CF_3 \cdot C(OH)(CH_3) \cdot CH_2 \cdot CO \cdot CF_3$	5.920	51.14	50.86	+0.28
	4.795	50.64		—0.22
Tetrafluoroethylene C_2F_4	3.345	76.04	76.00	+0.04
	4.150	72.26		+0.26

The results obtained are given in Table 3.

SUMMARY

On the basis of the macro method suggested by P. N. Fedoseev and M. Ia. Sobko, a micro method has been developed for the determination of bromine and iodine in organic compounds. It has been established that it is possible to use this micro method for the determination of fluorine in organic compounds, the com-

bustion products being absorbed with distilled water. The micro method developed can be used for both low molecular weight organic compounds, and for halogenated polymers which are difficult to burn.

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* In Russian.

** Original Russian pagination. See C.B. Translation.

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POLAROGRAPHIC DETERMINATION OF FORMIC ACID

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The work described in the present article was devoted to a study of the polarographic behavior of formic acid, and to establishing whether or not the polarographic method can be used for determining formic acid and its salts in solution.

Measurements were carried out on a U-301 Heyrovsky recording polarograph with a mirror galvanometer. The sensitivity of the galvanometer without a shunt (S^0) was 4.44×10^{-9} amp/mm, at a distance of 0.9 meters. The dropping electrode and electrolyzer were of the type suggested by Heyrovsky [1]. The capillary characteristics were $m = 1.49$ mg/sec^{-1}; $t = 3.31$ sec; $m^{2/3} \cdot t^{1/6} = 1.592$ mg$^{2/3}$sec$^{-1/2}$. The anode was a mercury pool whose potential when measured with respect to the normal calomel electrode was found to be +0.060 volt.

Preliminary experiments showed that it is possible to get polarograms for formic acid in weakly acid solutions. The most suitable supporting electrolyte was found to be 0.1 N sodium or potassium chloride acidified with hydrochloric acid. Reduction of formic acid starts at 1.7-1.8 volts (relative to the normal calomel electrode); large maximum peaks were obtained on the polarogram in the region of the limiting current. Since these maxima were very difficult to suppress it may be supposed that this has been the reason for the fact that the polarographic behavior of formic acid has not hitherto been studied.

Ideas developed by one of the authors of this article [2] regarding the role of the null discharge potential in irreversible electrochemical processes, and the scale of φ-potentials * suggested on the basis of these ideas, enabled us to cut down the number of substances among which it is necessary to seek for additives to suppress the polarographic maxima.

The nature of the additives adsorbed on the electrode surface depends on the value of the φ-potential. Preferential adsorption will be shown by: in the case $\varphi < 0$, additives of a cationic type; in the case of $\varphi > 0$ additives of an anionic type, and in the case of $\varphi = 0$, additives of the molecular type. Under the conditions used for studying the polarographic behavior of formic acid $\varphi < 0$.** Consequently, in order to suppress maxima in this particular case, one should look for additives of the cationic type.

Of the many cationic surface-active materials we tested the most suitable proved to be tribenzylamine — $(C_6H_5CH_2)_3N$. Tribenzylamine can suppress the maxima completely when a few drops of a saturated solution of this compound is added to 10 ml of a solution containing not more than 0.1 g mole/liter of formic acid; under these conditions, the pH of the test solution should be of the order of 2-4.

It is essential to point out that for each value of the pH of the solution, there is a permissible maximum concentration of formic acid for which it is still possible to get normal polarograms. Thus at pH 4 and pH 2, according to Fig. 1, the limiting concentrations of formic acid are equal to approximately 0.1 g mole/liter and 0.02 g mole/liter, respectively. Increasing the formic acid concentration beyond its limiting value, and also the use of solutions with pH < 2, lead to nonreproducible results. Under these conditions a visible film

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* φ-Potentials denote the shift in the stationary potential of the null discharge of the electrode metal.

** According to the latest results, the potential for the null discharge of mercury is equal to −0.19 volt [3].

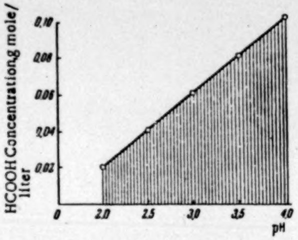

Fig. 1. Relation between the permissible concentration of formic acid and the pH of the solution during polarographic reduction of formic acid.

is formed on the mercury pool. Increasing the pH of the solutions beyond 4 is undesirable since subsequently, in order to maintain the value of the limiting current at a sufficiently high level, it is necessary to use comparatively high concentrations of formic acid. Tribenzylamine ceases to suppress the maxima and it also becomes impossible to obtain normal polarograms.

The shaded part in Fig. 1 corresponds to the values of formic acid concentrations for which it is possible to get normal polarograms.

Typical polarograms for formic acid in the absence and in the presence of tribenzylamine are shown in Figs. 2-4. In Fig. 5 are shown polarograms for the reduction of hydrogen ions at various pH values of the solution.

Results of the polarographic investigations showed that reduction of hydrogen ions accompanies reduction of formic acid.

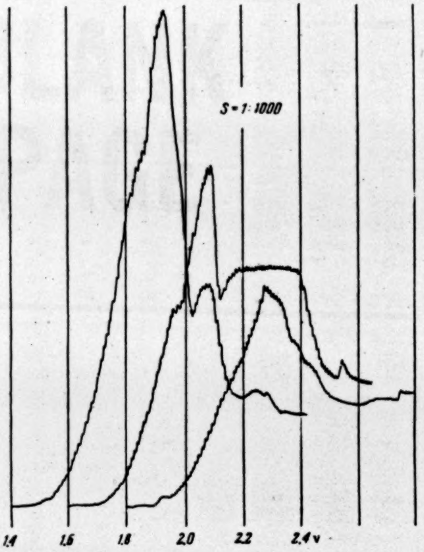

Fig. 2. Polarograms for formic acid in the absence of tribenzylamine.

The value of the limiting current increases on increasing the concentration of both the formic acid and the hydrogen ions. It is clear from Fig. 6 that with decreasing formic acid concentration the value of the

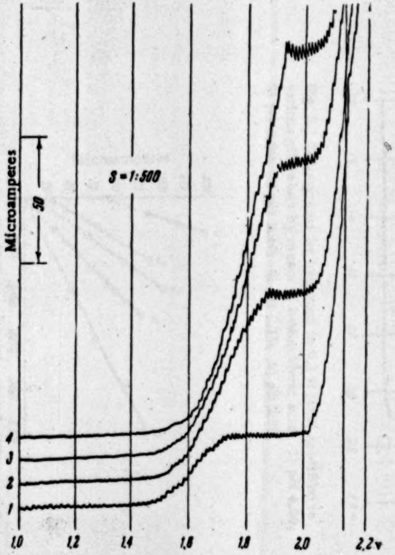

Fig. 3. Polarograms for formic acid at pH 2.46; 1) "Blank" (0.1 N NaCl); 2) 0.011 g mole/liter; 3) 0.022 g mole/liter; 4) 0.033 g mole/liter.

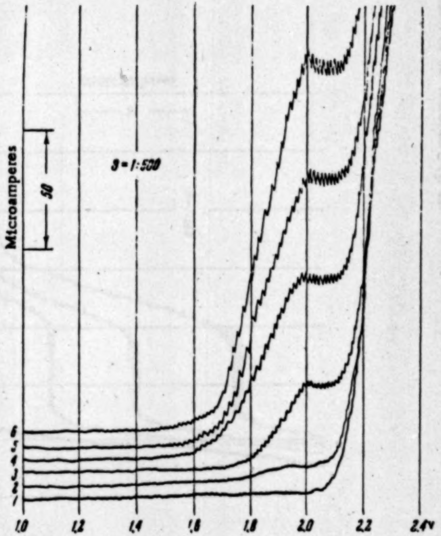

Fig. 4. Polarograms for formic acid at a constant concentration (0.11 g mole/liter) and at various pH values of the solutions; 1) pH 5.00; 2) pH 4.00; 3) pH 3.00; 4) pH 2.40; 5) pH 2.15; 6) pH 2.00.

total limiting currents approximates to the values of the limiting current for hydrogen at the given pH values of the solutions (Fig. 7). If the values corresponding only to the limiting currents of formic acid (excluding the limiting currents for hydrogen) are plotted along the ordinate instead of the value of the total limiting currents, then we get a linear relation between the concentration of the formic acid and its limiting current at various pH values of the solutions (Fig. 8).

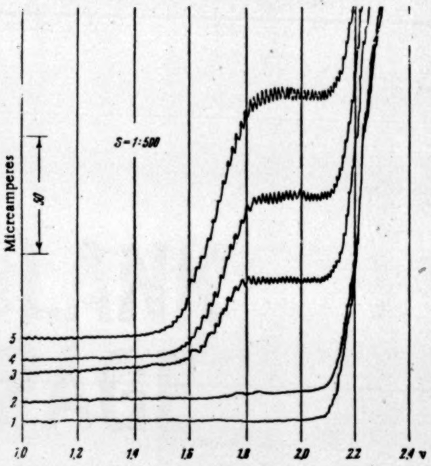

Fig. 5. Polarograms for hydrogen in 0.1 N NaCl acidified to various pH values by means of hydrochloric acid: 1) pH 4.00; 2) pH 3.00; 3) pH 2.40; 4) pH 2.15; 5) pH 2.00.

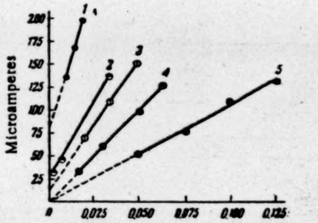

Fig. 6. Relation between the total limiting current and the concentration of formic acid at various pH values: 1) pH 2.00; 2) pH 2.46; 3) pH 3.00; 4) pH 3.50; 5) 4.00.

Thus the total limiting current is the sum of the limiting currents for the reduction of formic acid and of hydrogen ions. With increasing pH the limiting current which corresponds to reduction of hydrogen ions decreases, and starting at pH 3 and S = 1 : 500, is almost not recorded on the the polarograms. In Fig. 9, as an example are shown polarograms taken at pH 3.5 and S = 1 : 500 for various formic acid concentrations. In this case it can be considered that the limiting current is almost completely determined by the formic acid concentration.

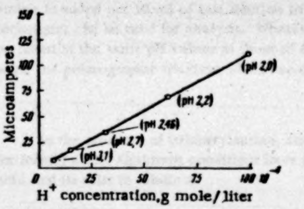

Fig. 7. Relation between hydrogen ion concentration and the limiting current.

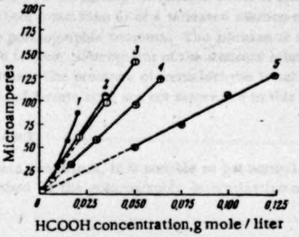

Fig. 8. Relation between formic acid concentration and the limiting current at various pH values of the solution: 1) pH 2.00; 2) pH 2.46; 3) pH 3.00; 4) pH 3.50; 5) pH 4.00.

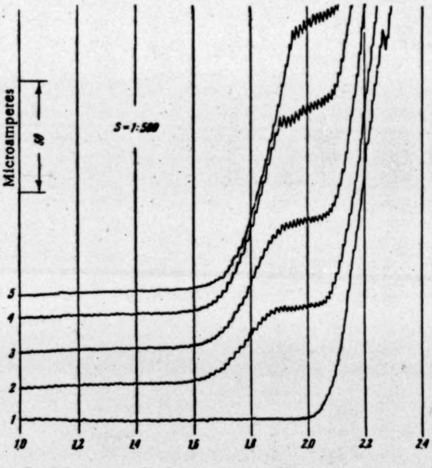

Fig. 9. Polarograms for formic acid at pH 3.5: 1) "Blank" solution (0.1 N NaCl); 2) 0.0165 g mole/liter; 3) 0.0302 g mole/liter; 4) 0.0505 g mole/liter; 5) 0.0640 g mole/liter.

On the basis of what has been said above the following procedure is proposed for the polarographic determination of formic acid and its salts in solution.

An aliquot of test solution containing not more than 0.05-0.06 g mole/liter of formic acid is acidified to a definite pH value of 3-4; polarograms are then taken in a supporting electrolyte of 0.1 N sodium or potassium chloride, using a sensitivity of 1 : 500. A few drops (not more than 6) of a saturated solution of tribenzylamine is added per 10 ml of test solution to suppress the polarographic maxima. The addition or comparison techniques can be used for analysis. Whatever technique is used, polarograms of the standard solutions should be taken at the same pH values as those of the test solution. The presence of formaldehyde is not desirable, since the polarographic maxima which are characteristic of formic acid are not suppressed in this instance.

SUMMARY

In the presence of tribenzylamine, and under certain conditions, it is possible to get normal polarograms for formic acid. Optimum conditions have been established for the polarographic determination of formic acid and its salts in solution.

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A NEW METHOD FOR THE DETERMINATION OF MICRO AMOUNTS OF CITRIC ACID

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A number of photometric methods have been proposed for the determination of microgram amounts of citric acid. The most sensitive and specific of these methods are based on the color reactions of pentabromoacetone [1-5]. The latter is formed from citric acid during treatment of the latter with oxidizing agents (permanganate is the most often used) in mineral acid media and in the presence of bromine [6]:

$$\begin{gathered} HOOC\cdot CH_2\cdot C(OH)(COOH)\cdot CH_2\cdot COOH + \\ + O(KMnO_4) \rightarrow \underset{\text{acetone dicarboxylic acid}}{OC(CH_2\cdot COOH)_2} + CO_2 + H_2O \end{gathered} \tag{1}$$

$$\underset{}{OC(CH_2COOH)_2} + 5Br_2 \rightarrow \underset{\text{pentabromoacetone}}{CBr_3\cdot CO\cdot CHFr_2} + 2CO_2 + 5HBr \tag{2}$$

We have established that pentabromoacetone is formed in high yield during electrolysis of citric acid on lead anodes using as anolyte sulfuric acid containing bromine ions.*

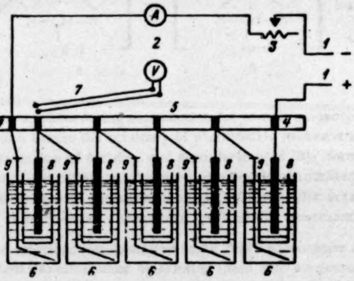

Fig. 1. Diagram of the apparatus: 1) Terminals connecting the apparatus to a dc source; 2) measuring apparatus; 3) rheostat; 4) plug socket for leading current to the terminals of the cathodes; 5) terminal junction for series connection of the five electrolytic cells (or parts of them); 6) electrolytic cell; 7) voltmeter contacts for connecting to the electrolytic cells; 8) anodes; 9) cathodes.

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*Pentabromoacetone is not formed during electrolysis in acetic, phosphoric, or nitric acids. Under such conditions, the electrodes are not covered with lead dioxide, and the latter presumably is of significance for the electrosynthesis of pentabromoacetone.

A schematic diagram of the apparatus used for the electrolytic conversion of citric acid is shown in Fig. 1. A maximum and almost constant yield of pentabromoacetone is obtained for a certain value of the acidity of the electrolyte in the anode compartment (anolyte), for appropriate values of the current and voltage. Temperature changes from 20-40° do not appreciably affect the electrochemical process. The highest yield of pentabromoacetone is obtained in 2 N sulfuric acid containing 11 mg of potassium bromide, with a current of 0.2 amperes and a voltage of 3.0 volts. In this case the volume of the anolyte was 5 ml while the area of the working surface was 10.5 to 11.5 cm^2; this corresponded to an average current density of about 1.8 amperes/dm^2. Under these conditions, the duration of electrolysis was 45 minutes. The pentabromoacetone formed in the apparatus was determined by the highly sensitive Fujiwara reaction* (pyridine in a strongly alkaline medium [2, 7, 10, 18]).

Results of some special tests indicated that synthesis of the "dye" may proceed according to the following reactions:

$$CBr_3\cdot CO\cdot CHBr_2 \xrightarrow{+NaOH} CHBr_3 + CHBr_2\cdot COONa \qquad (3)$$

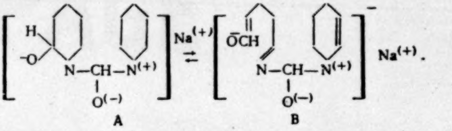
$$CHBr_3 + NaOH \rightarrow \rangle CBr_2 + NaBr + H_2O \qquad (4)$$

methylene bromide

$$\rangle CBr_2 + 2C_5H_5N \xrightarrow{+NaOH} \text{colored compound} \qquad (5)$$

(dye)

The most probable structure of the "dye" corresponds to the anion of the sodium salt (aci-salt) of the betaine of hydroxydihydropyridinemethinylpyridine (formula 6 A) or its tautomeric alicyclic form (formula 6B):



(6)

The cherry-red color which appears during the reaction for pentabromoacetone in the anolytes is partially masked by a yellow tinge which lowers the accuracy of photometric measurements. It has been found that this tinge is the result of the interaction of pyridine and persulfuric acid [8]; formation of the latter is catalyzed by bromine ions [9]. The effect of persulfuric acid can be completely eliminated by successive treatment of the reaction mixture after electrolysis with potassium bromide, sulfosalicylic acid, and potassium ferrocyanide. The intensity of the cherry-red color does not change as a result of this treatment.

The optical density of the solutions was measured on an "FM" photometer (with green filter S-53),** while the turbidity of the solutions was eliminated by diluting them with an acetone-ammonia mixture; the color was stabilized by addition of a drop of concentrated alkali. Despite this, the optical density of the solutions still decreased gradually (mainly because of the effect of atmospheric carbon dioxide). Accordingly, photometric measurements were made not later than 15 minutes after formation of the colored compound, and during determination of a series of solutions the least colored solutions were measured first.

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* No information has yet been published regarding the nature of the processes occurring during this reaction, nor has the composition of the cherry-red colored compound been established.

** The "FEK" photocolorimeter is not quite so suitable, nor is the method of standard solutions.

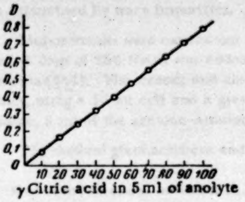

Fig. 2. Calibration curve.

During electrolysis of from 10 to 100 γ of citric acid, the optical density of the solutions obtained is proportional to the citric acid concentration of the anolyte (Fig. 2). Some of the acid presumably is oxidized further, since the optical density amounts to 80% of the values obtained with equivalent amounts of pure pentabromoacetone.

1. Construction of a Calibration Curve

Into the anode cells (Fig. 3) removed from the apparatus were measured 4-ml lots of standard solutions containing from 10 to 100 γ of citric acid. To these lots of standard solutions were added 0.5 ml of 20 N sulfuric acid, 0.4 ml of 0.33 N potassium bromide, and the volumes of the anolytes made up to 5 ml with distilled water. Lead electrodes * which had been mechanically cleaned to the polished metal surface were immersed in the anode cells, and the whole immersed in the catolyte – 1 N sulfuric acid. Catolyte and anolyte should be at the same level. The apparatus was connected to the dc supply and electrolysis carried out at 0.2 amperes and 3.0 volts.

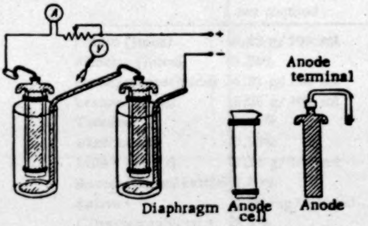

Fig. 3. Electrolytic cells (on the left) connected in series, and an anode cell (on the right) made of glass tubing (8 × 1.5 cm) with a cellophane diaphragm, fastened with a rubber ring; lead anode with terminal (11 × 0.13 × 0.2 cm).

TABLE 1

Determination of Citric Acid in Standard Solutions

Taken, in γ	Found (mean of five determinations), in γ
30.0	30.8
40.0	41.7
50.0	50.0
60.0	58.8
70.0	69.5
80.0	78.0
90.0	90.7
100	99.5

At the end of 45 minutes, the anode cells (together with the electrodes) were removed from the apparatus. Without removing the anodes, 0.5-ml lots of potassium bromide (24 g/100 ml) were added to the liquids. After standing for 5 minutes, the free bromine liberated was bound by means of 0.75 ml of 0.55 M sulfosalicylic acid. At the end of one minute, 0.1-ml lots of 0.48 N $K_4Fe(CN)_6$ solution were added to the completely colorless liquids. The slightly yellowish solutions were poured into 20-40-ml test tubes with ground glass stoppers.**

Each anode cell with its electrode was washed out with 3 ml of pyridine. The latter was then quantitatively combined with the main liquid, and 8 ml of sodium hydroxide solution (100 g NaOH in 150 ml water) added to each tube; the whole mixture in each tube was then thoroughly shaken for 20-30 seconds, and heated for 3 minutes in a bath at 80°. The heated tubes were all withdrawn simultaneously from the bath and cooled immediately in an ice bath. The pyridine layers acquired colors ranging from rose to cherry-red according to the citric acid concentration. In the control which did not contain citric acid, the color should only be a weak rose determined by trace impurities.

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* Prepared from pure sheet lead.

** In order to avoid loss it is advisable to use the anode for directing the stream of anolyte into the tubes.

Measurements were carried out by transferring 2 ml of the colored, turbid pyridine layer into a 10-ml tube. A drop of 25% NaOH was added to this aliquot, followed by 5 ml of a mixture of acetone and concentrated ammonia (4 : 1). The mixed, and absolutely colorless solution was photometrically measured on an "FM" apparatus, using a 10-ml cell and a green S-53 filter. The reference solution was one composed of 2 ml of pure pyridine, 5 ml of the acetone-ammonia mixture, and a drop of alkali solution.

The method gives accurate and reproducible results (Table 1).

2. Determination of Citric Acid in Certain Biogenous Materials and in Medicinal Preparations

Using the method developed, citric acid was determined in a number of animal and plant materials, and also in medicinal preparations.

TABLE 2

Quantitative Determination of Citric Acid in Some Biogenous Materials and Medicinal Preparations

Test material	Citric acid found		Citric acid content according to literature, %
	our method	comparison method	
Potato (juice)	0.42 g/100 ml	0.40 g/100 ml••••	0.52 [10-13]
Bilberry (juice)	0.96%	0.89% •••••	0.91 [12]
Pomegranate (juice)	4.37 g/100 ml	4.18 g/100 ml•••••	5-9 [13, 14]
Lemon (juice)	6.26 g/100 ml	5.83 g/100 ml•••••	5-7 [13, 15]
Tomato	0.85%	0.65%•••••	0.61 [12, 13]
Mushrooms•	0.23%	0.20% ••••	0.35 [12]
Milk• (cow's)	0.14 g/100 ml	0.12 g/100 ml•••••	0.18-0.25 [13-16]
Bones• (horned cattle)	0.50%	0.44%•••••	Up to 1.6 on the dry weight
Saliva•	1.09 mg/100 ml	0.48 ml/100 ml•••••	0.1-5.0 mg/100 ml [13]
Citramon tablets••	3.1%	3.29%	~4
"Novomigrophen" tablets •••	2.98%	3.21%	~3

• Proteins were precipitated beforehand.

•• Contained citric acid, aspirin , phenacetin, caffeine, and cocoa.

••• Contained citric acid, phenacetin, caffeine, pyramidone, and starch.

•••• Taussky and Shorr method [17].

••••• Taylor's method [18].

Numerous components of the biosubstrate will be found in the plant and animal samples and, accordingly, in the anolyte. In separate experiments it was established that after electrolysis and the pyridine reaction, 100 γ of the following compounds did not give a color: arginine, ascorbic acid, acetone, alanine, acetylcholine-iodide, aspartic acid, allantoin, alloxane, acetaldehyde, glycine, glucosamine, guanidine, inositol, glycerophosphoric, glutamic, levulinic, maleic, lactic, uric, and nicotinic acids, urea, caffeine, xanthine, creatine, creatinine, pyruvic acid, hydrogen cyanide, pectin, thiamine, acetic acid, fructose, furfurol, formaldehyde, ethanol, and succinic acid.

The compounds listed below give a color equivalent to 10-40 γ citric acid: tyrosine, histidine, adrenaline, phenylpyruvic acid, butyric acid, phenol, quinic acid, hydroquinone, pyrocatechol, phenylalanine, tryptophane, crotonic acid. In addition, a color was observed in the case of acetoacetic, malonic, β-hydroxymalonic, and malic acids.

Despite the fact that some of the compounds listed above were found in the test natural objects, determination of citric acid was always selective (for results, see Table 2). This is partly explained by their removal during the procedure used (see below), and also by the considerably dilution.

Procedure for Determination of Citric Acid in Biogenous Substrates. The components of the biosubstrate in a number of objects did not lower the specificity of the determination. Aliquots of such objects in the form of extracts or juice were diluted with water until the citric acid concentration was 10-100 γ citric acid in 4 ml. The procedure followed subsequently was the same as that used for determination of citric acid in its pure aqueous solutions. In some cases more accurate results were obtained by precipitating proteins beforehand in aliquots of test material* (See Table 3).

Reference solutions used for the analysis were prepared as follows. Into a 20-30-ml test tube was measured out a volume of test solution equal to that introduced into the anolyte. To this test tube was added 1.0 ml of 10 N sulfuric acid, 0.1 ml of potassium bromide solution (24 g/100 ml), 0.1 ml of potassium bromate (0.5 g/100 ml), and the solution diluted to 5 ml with distilled water. The subsequent treatment of this solution was carried out simultaneously with the preparation of the anolytes for the color reaction after the anolytes had been electrolyzed.

TABLE 3

Preparation of Plant and Animal Material for Citric Acid Determination

Test material		Final dilution of extract or aliquot		Extract taken for determination, ml	
		without precipitation of proteins	after precipitation of proteins	without precipitation of proteins	after precipitation of proteins
Potato	Juice tested	1 : 100		2.0	
Bilberry		1 : 500		3.0	
Pomegranates		1 : 2000		2.0	
Lemons		1 : 2000		2.0	
Tomatoes	The sample was grounded up with water, and the extract filtered through a glass filter	1 : 4000		2.0	
Mushrooms	The sample was ground with water and left to stand for about one hour		1 : 16		0.25
Milk (cow's)	Whole milk was diluted with water in the ratio of 1 : 10		1 : 40		1.00
Bones (horned cattle)	The samples of dry, degreased bone flour was heated with 5% HBr		1 : 100		1.50
Saliva (human	The proteins were precipitated and the protein-free centrifugate evaporated to a volume equal to half of that of the sample of saliva originally taken				1.00

Note. The proteins were precipitated by adding a 10% solution of phosphotungstic acid to part of the sample until precipitate ceased to separate out. The precipitate was centrifuged. The clear centrifugate was diluted with water and an aliquot taken for analysis.

In contrast to the main solution, the reference solution usually remained colorless; sometimes, however, it had a rose color; the reference solution was used for the colorimetric measurements, the procedure outlined above for preparing the solutions for measurement being followed.

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*Of the materials generally used for precipitating proteins, trichloroacetic acid should not be used, since this compound gives a color with pyridine and alkali.

Procedures for Determination of Citric Acid in Citramon and Novomigrophen Tablets. The ground tablets were extracted three times with 10-ml lots of benzene. The insoluble residue was kept at 90° until the solvent had been removed by evaporation, and was then quantitatively transferred to a 500-ml standard flask; 20 ml of 1 N sulfuric acid was then added and the solution made up to the mark with water. After the flask had been shaken and the turbidity allowed to settle, 2 ml of the solution was taken for determination, the same procedure as that outlined for determination of citric acid in its pure solutions being followed.

SUMMARY

A new method for the determination of 10-100 γ of citric acid has been developed, which is based on its conversion into pentabromoacetone on a lead anode, with a subsequent photocolorimetric determination based on the color formed by the interaction of pentabromoacetone with pyridine and alkali. The method permits a fairly rapid and selective determination of citric acid in various vegetables, berries, fruits, in bones, saliva, and milk, and also in medicinal preparations.

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PHOTONEPHELOMETRIC DETERMINATION OF VITAMIN B_1 (THIAMINE)

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A large number of methods have been developed for the quantitative determination of vitamin B_1 (thiamine) in pharmaceutical preparations and other materials [1-14]; all the same, many of these methods are not suitable for practical purposes. We have developed a rapid photonephelometric method which is based on the fact that thiamine is completely precipitated from solution at pH 4.5-5.5 by phosphotungstic acid. The method is applicable to the determination of thiamine in injection solutions, yeast, and some medicinal mixtures. The limit of identification for thiamine hydrochloride is 2 γ in 1 ml of reaction mixture.

The stock solution used was a 5% solution of crystalline thiamine hydrochloride.

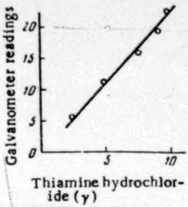
Nephelometric measurements were carried out on a V. E. Nize type photonephelometer, with a differential setup with two selenium photoelements and electrical compensation. The sensitivity of the mirror galvanometer was 1×10^{-8} amperes/division. Voltage variation in the circuit within the limits 80-150 volts was stabilized with a ferroresonance stabilizer having a power of 14 watts; the capacity of the cell was 35 ml.

After establishing the optimum conditions for precipitating thiamine and obtaining a turbidity suitable for quantitative measurements, the following method was developed.

The calibration curve was constructed as follows: known volumes of a 0.05% solution of thiamine hydrochloride (0.2, 0.5, 0.7, 1.0, 1.5 ml) were introduced by means of a micropipet into 50-ml flasks; water was then added to each flask in such amount as to leave room for the addition of 1 ml of 0.01 M sodium phosphotungstate and – if necessary – the volume made up accurately to the mark with water. The contents of the flasks were transferred to 100-ml conical flasks, the whole shaken up thoroughly and nephelometric measurements carried out. The readings obtained on the nephelometer after 5 minutes were then used for constructing a calibration curve. Not more than 30 minutes are usually required for constructing such a curve.

Thiamine hydrochloride was determined in 5% injection solutions as follows: 1 ml of test solution was diluted to the mark with distilled water in a 100-ml standard flask; 0.5 ml of this solution was transferred to a 50-ml standard flask, and distilled water added in such amount as to leave room for addition of 1 ml of 0.01 M sodium phosphotungstate; after the latter had been added, the volume was then made up to the mark with distilled water. The contents of the 50-ml flask were then transferred to a 100-ml conical flask where they were thoroughly shaken up and nephelometric measurements carried out.

Determination of the Thiamine Content of Yeast and Medicinal Mixtures. Since vitamins A, B_2, C, D, and PP, which enter into the composition of yeast, are not precipitated by sodium phosphotungstate, thiamine can be determined in this material as follows. The total weight of sample submitted for analysis was determined and a fifth of this amount taken. When the amount of sample available was less than 15 g, then the whole amount was taken for thiamine determination. Weighing was carried out on a technical-chemical balance. The mean weight of one sample of yeast taken from several dozens was determined. The material taken for analysis was ground up in a porcelain mortar until a homogeneous powder was obtained. Two lots of 5 g of this powder were weighed on an analytical balance, and each lot dissolved in distilled water in two 50-ml flasks. From each flask 12.5 ml was pipetted out into 50-ml standard flasks when the yeast contained about 2 mg of thiamine, while 25-ml lots were pipetted out when the thiamine content was 1 mg. The subsequent procedure followed was the same as that described for 5% injection solutions. Determination can also be carried out on one sample of yeast.



Calibration curve for thiamine determination.

Of the various materials contained in medicinal preparations only pyramidone interferes with thiamine determination. In such cases a sample of the powder merely treated 3-4 times with 5-ml lots of chloroform on a filter paper contained in a funnel. The pyramidone passed into the filtrate. The thiamine remained on the funnel (the solubility of thiamine in chloroform is 1 : 200,000 [1]) together with ascorbic acid. The residue on the funnel was treated several times with water and the filtrates collected in a 100-ml standard flask; the volume was made up to the mark with water and the whole thoroughly mixed; 1 ml of this solution was transferred to a 50-ml standard flask and the procedure outlined above followed.

Preparation	Composition, in g	Thiamine found, in g	Error, in %
Yeast	Thiamine 0.00200 Sugar 0.024480	0.00194	3
Yeast	Thiamine 0.00100 Ascorbic acid 0.02500 Vitamin B_2 0.0010 Vitamin A 1650 Sugar	0.00095	5
Yeast	Thiamine 0.00100 Ascorbic acid 0.02500	0.00096	4
Injection solution	Thiamine 5%	4.9	2
Powder	Thiamine 0.00200 Nicotinic acid 0.02 Ascorbic acid 0.05 Glucose 0.5	0.00196	2
Powder	Thiamine 0.050 Ascorbic acid 0.1 Pyramidon 0.8	0.048	4

The results given in the Table show that the method developed permits determination of small amounts of thiamine in mixtures with reasonable accuracy.

SUMMARY

A method which has been developed for the determination of thiamine (Vitamin B_1) in preparations turned out by the vitamin industry, and in medicinal preparations, is based on precipitation of thiamine by sodium phosphotungstate. The experimental error does not exceed 5%. The limit of identification is 2.5 γ of thiamine hydrochloride in 1 ml of reaction mixture.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF DIMETHYLPHENYLCARBINOL

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Determination of tertiary alcohols by the usual esterification methods with acetic anhydride, phthalic anhydride, or acetyl chloride always leads to low results, since under the conditions used for esterification they are partially dehydrated. The general method of Mitchell and Smith [1] is also inapplicable, since in our case it was necessary to determine dimethylphenylcarbinol (DMPC) in mixtures with phenol and acetophenone, which, during acetylation in the presence of boron trifluoride, react with the water liberated. The method based on hydrochlorination of DMPC, followed by decomposition of the chloride with alkali, and determination of chloride ions with silver nitrate is exceedingly long. For the same reasons, under production conditions the method according to which DMPC is quantitatively dehydrated, while the α-methylstyrene formed is determined by means of mercuric acetate in methanolic solution, is also inapplicable.

In order to find an analytical method for the quantitative determination of DMPC which is reliable enough, and is readily carried out under production conditions, the work described here was undertaken. The method selected was based on two processes: a) dehydration of DMPC, and b) titration of the water liberated with Fischer reagent. Chief attention was given to developing the conditions for quantitative dehydration of DMPC.

In order to study the percentage dehydration of the carbinol under various conditions, an aliquot of catalyst (cupric sulfate, boron anhydride, sulfuric acid, and sodium bisulfate) was introduced into a 100-ml flask fitted with a ground glass stopper; this was followed by 10 ml of isopropylbenzene as solvent for DMPC, and an aliquot (0.1-0.3 g) of the test carbinol. The flask was connected to a reflux condenser and heated for 10-60 minutes. The condenser was then washed down with another 10 ml of isopropylbenzene, and the whole cooled to room temperature. Then, by means of a pipet and without disturbing the deposit of catalyst, a sample (10-15 ml) of the liquid in the flask was transferred to another similar flask and titrated with Fischer reagent. A blank was carried out in parallel using the same conditions and reagents but omitting the carbinol.

TABLE 1

Wt. of DMPC, g	Wt. of sodium bisulfate, g	DMPC determined, g	DMPC determined, %	Wt. of DMPC, g	Wt. of sodium bisulfate, g	DMPC determined, g	DMPC determined, %
0.920	0.1	0.898	97.7	0.0824	0.2	0.0824	100.0
0.1068	0.1	0.1003	94.0	0.1578	0.2	0.1571	99.6
0.1534	0.1	0.1489	97.0	0.1672	0.2	0.1666	99.7
0.1784	0.1	0.1717	96.2	0.1854	0.2	0.1872	101.0
0.0664	0.2	0.657	99.0	0.1882	0.2	0.1882	100.0

It was established that the maximum percentate dehydration of DMPC in the presence of cupric sulfate as catalyst did not exceed 28%, while it was 26% in the case of boric anhydride and sulfuric acid. The highest percentage dehydration of 92% was achieved on adding 2 drops of concentrated sulfuric acid. When the concentrated acid was used, the mixture was only heated to 85° and was kept at this temperature for 15 minutes; at higher temperatures resinification occurred which interfered with titration.

Dehydration of DMPC in the presence of sodium bisulfate was appreciably better; no resinification was observed. This permitted the temperature to be increased almost to the boiling point of the isopropylbenzene. In order to avoid loss of water, the contents of the flask were not boiled but only brought up to incipient boiling (152°). The sample was kept at this temperature for 10 minutes.

As can be seen from Table 1, quantitative dehydration of DMPC was achieved on using 0.2 g of sodium bisulfate.

In order to study the effect of impurities on the accuracy of determination of DMPC, experiments were carried out on its dehydration in the presence of phenol, dimethylphenylparacresol, acetophenone, and α-methylstyrene; DMPC was determined initially in the presence of each of these compounds taken separately, and then in mixtures of these compounds. In all cases, 0.2 g of sodium bisulfate was added; heating was carried out at 152°, the sample being held at this temperature for 10 minutes.

TABLE 2

Weight of DMPC in g	Impurity		DMPC found, in g	DMPC determined as % of that taken
	Nature of impurity	Weight, in g		
0.1162	Phenol	0.2288	0.1162	100.0
	Acetophenone	0.3452		
	DMPPC	0.2140		
0.1284	Phenol	0.7332	0.1276	99.3
	Acetophenone	0.1060		
	DMPPC	0.2028		
0.1180	Phenol	3.3122	0.1168	99.0
	Acetophenone	0.4480		
	DMPPC	0.1712		
0.2276	Phenol	0.2768	0.2248	99.8
	Acetophenone	0.3570		
	DMPPC	0.1372		
	α-Methylstyrene	0.1868		
0.1218	Phenol	0.3020	0.1206	98.9
	DMPPC	0.2885		
	Acetophenone	0.2196		
	α-Methylstyrene	0.1989		

From the results given in Table 2 it is obvious that phenol, dimethylphenylparacresol (DMPPC), acetophenone, and α-methylstyrene, present as impurities, do not interfere with determination of DMPC.

SUMMARY

A method has been developed for the quantitative determination of dimethylphenylcarbinol in industrial mixtures. Phenol, dimethylphenylparacresol, acetophenone, and α-methylstyrene do not interfere.

The experimental error is about 1%. A single determination does not take more than 25 minutes.

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THE PHOTOMETRIC DETERMINATION OF ZINC

A. I. Krupkin and L. A. Zhechkova

Modern photoelectric apparatus guarantee such a high degree of accuracy for the measurement of light absorption that it is possible to carry out photometric determinations of large amounts of an element, for example up to 15% of zinc. We have developed an indirect method for determination of zinc which is based on its precipitation [1-4] as $(C_{13}H_{17}ON_3)_2 \cdot H_2[Zn(SCN)_4]$, with subsequent formation of molybdenum blue by partial reduction of phosphotungstomolybdic acid with pyramidon.

Pyramidon was determined colorimetrically by measuring out 2-10 ml of pyramidon solution (1.13 mg/ml) – corresponding to 0.1-0.5 mg of zinc oxide – into a 100-ml standard flask, and adding 70-80 ml of water, and 10 ml of phosphotungstomolybdic acid, and making up to the mark with water. The solutions to be poured together and the water were warmed to 20° beforehand. The solution obtained was then kept for 1.5 hours at 20°.

The phosphotungstomolybdic acid was prepared as follows [5]: 0.4 g of ammonium phosphomolybdate and 20 g of sodium tungstate were boiled for 2 hours with 10 ml of 87% phosphoric acid and 150 ml of water under reflux. On cooling, the solution was diluted with water to 200 ml and filtered.

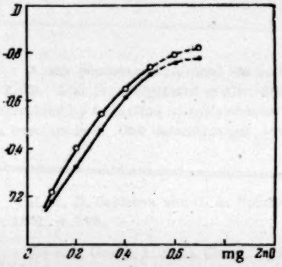

Fig. 1. Calibration curves for the photoelectric colorimeter FEK-M: O – By titration of pyramidon solution; ● – after precipitation of zinc from the solution to be titrated in the form of $(C_{13}H_{17}ON_3)_2 \cdot H_2[Zn(SCN)_4]$.

The optical density was measured after 1.5-3 hours in 20-mm cells using a red filter. Control cells were filled with water.

Zinc was precipitated by mixing the test solution, pyramidon and potassium thiocyanate in the presence of acetic acid [1-4]. The precipitate formed is readily soluble; the choice of a wash liquor presented difficulty. As our experiments showed, amyl acetate was suitable for this purpose.

The total volume of the solution during precipitation, duration of precipitation, and precipitation temperature are of importance for the quantitative precipitation of zinc.

A twelve-fold excess of sodium, potassium, magnesium, calcium, aluminum, and antimony, taken either separately or together, do not interfere with determination of 0.1 mg of zinc oxide. On increasing the amount of zinc oxide to 0.5 mg, the same cations do not interfere appreciably when present in amounts which are twice that of zinc. No tests were carried out with greater amounts of impurities. Barium, lead, and trivalent iron interfere with zinc determination; barium and lead are removed as the sulfates.

Before determination of zinc, the precipitant for zinc is prepared; for this purpose equal parts of a 4% solution of pyramidon and a 50% solution of potassium thiocyanate are mixed; to this mixture is added glacial acetic acid on the basis of 0.3 ml acetic acid per 20 ml of mixture. 5 ml of test solution containing 0.1-0.5 mg of zinc oxide* is measured into a special beaker fitted with a nozzle and a ground glass stopper (e.g. 60-mm tall, 30-mm diameter), 2 ml of precipitant solution is then added and the whole mixed. The beaker is covered and kept in a thermostat for 2-3 hours at 30 ± 1°. The precipitate is then filtered off under vacuum and washed 5 times with amyl acetate, the latter being taken in 1-ml portions. The amyl acetate remaining is removed by heating the beaker on a boiling water bath.

The precipitated zinc salt is dissolved in hot water and transferred to a 100-ml standard flask, in which it is made up to 70-80 ml with water; the pyramidon is then determined as described above.

The calibration curves are shown in the figure.

The results obtained are always low. This, however, does not prevent determination of zinc with an accuracy of 0.1-0.3% (by weight).

For zinc contents greater than 0.5 mg in the test solution the method is not applicable. Good results were obtained for the determination of zinc in glass. (See Table).

Determination of Zinc in Glass

Zinc added, in terms of ZnO, %	ZnO found, %					Error, %
	Determinations					
	1	2	3	4	Mean	
0.93	1.06	1.10	—	—	1.08	+0.15
1.56	1.47	1.53	—	—	1.50	—0.06
5.05	4.88	5.08	4.95	5.05	4.98	—0.07
6.58	6.48	6.32	6.36	6.30	6.37	—0.21
10.25	10.24	10.16	10.28	10.32	10.25	0
14.96	14.85	15.15	—	—	15.00	+0.04

SUMMARY

A new photometric method has been developed for the determination of up to 15% of zinc (calculated as ZnO). Zinc is precipitated as zinc dipyramidontetrathiocyanate, and the pyramidon content of the latter determined by formation of molybdenum blue from phosphotungstomolybdic acid. The effect of other ions has been studied. One determination, without decomposition of the material, takes 4 hours.

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* 0.1-0.4 g of test material is taken depending on the expected zinc content. For silicates the amount of hydrofluoric acid used is 1-5 ml while the amount of nitric acid is 10-15 ml. If these amounts of zinc are contained in a smaller volume, then the latter is made up to 5 ml with water.

SPECTROGRAPHIC ANALYSIS BY THE EVAPORATION METHOD

COMMUNICATION 6. DETERMINATION OF CADMIUM, GERMANIUM, INDIUM, GALLIUM, GOLD, ANTIMONY, AND LEAD IN URANOUS-URANIC OXIDE[*]

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The principles of the evaporation method have been published previously [1-3], and the possibility has been demonstrated of determining B, Li, Mn and some other elements present as impurities in U_3O_8, Al_2O_3, ThO_2, and BeO which are of low volatility. The main condition which ensures the efficiency of the evaporation method is that there should be a large difference between the volatilities of the impurities to be determined and that of the main component. In order to increase the sensitivity of the determination, it is often necessary to modify the method of preparing the test sample (evaporation of impurity) and of carrying out the spectrographic analysis of the concentrates. The present article is devoted to the application of the evaporation method for determining a group of volatile elements (Cd, In, Ge, Ga, Au, Sb, and Pb) in uranous-uranic oxide. In the case under consideration, some difficulties arose during the determination of about 3×10^{-5}% of cadmium and indium.

The experimental setup used for evaporating the impurities has been described earlier [1]. Evaporation was carried out at atmospheric pressure, since on heating U_3O_8 in a vacuum, this oxide decomposes with formation of the more volatile uranium trioxide. Tests showed that during evaporation of cadmium oxide from the samples certain anomalies were observed. At a temperature of the graphite crucible of 1600-1700°, cadmium oxide evaporated intensively, and gave the impression that all the cadmium evaporated from the sample in the course of one minute, since repetition of the evaporation process at the given temperature did not lead to the deposition of cadmium on the electrode. Nevertheless, when the same sample of U_3O_8 was heated to a higher temperature (1900-2000°) cadmium was deposited on the electrode again. Spectrographic analysis of the condensate obtained by repeated evaporation at the higher temperature showed that the blackening of the spectrographic lines for cadmium was even greater than that obtained during analysis of the condensate obtained during the first minute of evaporation at a crucible temperature of about 1600°.

TABLE

Test element	Analytical line in A	Spectrograph used	Sample wt., in mg	Sensitivity in %
Cd	2265.02	ISP-22	200	$3 \cdot 10^{-5}$
In	4511.32	ISP-51	200	$3 \cdot 10^{-5}$
Ge	2651.17	ISP-22	200	$3 \cdot 10^{-5}$
Ga	2874.24	ISP-22	50	$3 \cdot 10^{-4}$
Au	2675.95	ISP-22	50	$3 \cdot 10^{-5}$
Sb	2311.47	ISP-22	200	$1 \cdot 10^{-3}$
Pb	4057.82	ISP-51	50	$3 \cdot 10^{-4}$

Thus, during evaporation of U_3O_8 samples containing cadmium as impurity, some processes occur which lead to partial combination of the cadmium in the sample. Accordingly, in order to avoid systematic errors it is essential to evaporate cadmium present as impurity at a temperature of about 2000°. This temperature is quite sufficient for ensuring that the oxides of all the other elements to be determined (In, Ge, Ga, Au, Sb, Pb) also evaporated, while it is still low enough to prevent appreciable evaporation of the U_3O_8 itself. In order to achieve the necessary degree of accuracy during determination of cadmium, indium, and antimony, 50 mg of U_3O_8 proved insufficient, and about 200 mg of the oxide had to be used. When a sample of this size was used the procedure adopted was to split it up into four lots of 50 mg, evaporating each lot of 50 mg separately and collecting all four condensates on one electrode; by following this technique the necessary increase in blackening of the spectrographic lines was achieved. This technique ensured the necessary sensitivity but it means of course that an analysis takes considerably longer.

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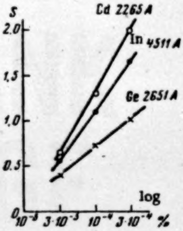
[*] For Communication 5 see Optics and Spectroscopy 3, 16 (1957).

Spectrographic analysis of the sublimate on the front surface of the electode was carried out using a condensed spark (generator IG-2; C = 0.012 μF; L = 0.15 mH). The inter-electrode distance was 2 mm. The accuracy of the electrode setting was established by means of a shadow projection. The most sensitive lines of the various test elements lie in various parts of the spectrum, accordingly it was found expedient to photograph the spectra simultaneously on two spectrographs (ISP-22 or Q-24 and ISP-51 with a focussing camera whose focal length was 270 mm). The analytical lines and some of the conditions used for carrying out spectrographic analysis of the sublimates are given in the Table.

In order to use the most sensitive line for indium – In I 4511.3 A – it was necessary to use silver electrodes, since on using copper electrodes, the intense copper line Cu 4509.5 A was superimposed on the analytical line for indium. In order to make use of the sensitive cadmium line Cd II 2265 A, photographing of the spectra in the ultraviolet was carried out on photographic plates "spectrographic, type III," which preserve their constrast and sensitivity in the far ultraviolet.



Calibration curves for the determination of Cd, Ge, and In in U_3O_8.

Analysis was carried out by the three-standards method. The standard mixtures were made up on the basis of pure samples of uranous-uranic oxide. The method of additions was also used for carrying out particularly important determinations. The mean square error for a single determination of any of the elements indicated did not exceed 15-20%, around the concentrations indicated in the Table. As an example, calibration curves for the determination of cadmium, indium, and germanium in uranous-uranic oxide are shown in the diagram.

The authors are indebted to A. N. Zaidel' for valuable advice and to G. G. Kuid for carrying out control tests.

SUMMARY

Cadmium and indium present as impurities in U_3O_8 do not volatilize completely when they are evaporated from the latter at 1600-1700°. In order to avoid systematic errors during the spectrographic determination of these two elements present as impurities in U_3O_8, it is necessary, therefore, to carry out evaporation at 2000°.

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* Original Russian pagination. See C.B. Translation.

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POTENTIOMETRIC TITRATION OF BENZOQUINONE IN MALEIC ACID SOLUTIONS

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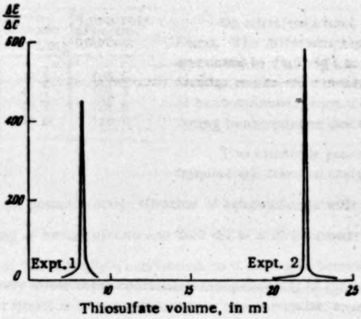
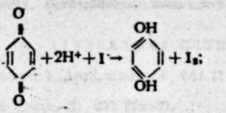
During the catalytic oxidation of benzene over a vanadium catalyst, in addition to the main reaction product – maleic acid – benzoquinone is also formed [1]; the quantitative determination of benzoquinone is of essential importance for the production control of maleic acid. Rzymkowski [2] tried to develop a reliable method of determining benzoquinone but he did not succeed in getting positive results.



For the potentiometric titration of the dark-orange colored solutions obtained, we used the usual iodometric method of determining benzoquinone [3].

1)



2)

$$I_2 + S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}.$$

When this method was used a well-defined potential jump was observed and good results were obtained; a complete determination takes a few minutes.

Since a compensation scheme is regarded as being more reliable [4], we used an LP-5 potentiometer;

the redox potential of the system being titrated was measured by means of a platinum electrode with respect to the saturated calomel electrode.

For benzoquinone contents of the order of 0.0005 mole the experimental error did not exceed 3% relative.

The benzoquinone used for the experiments was synthesized from hydroquinone [5]. The melting point of the benzoquinone recrystallized from benzene and purified by sublimation under vacuum (5 mm Hg) was 112.0-112.5°. 30-40% aqueous production liquors of maleic acid and benzoquinone * obtained by catalytic oxidation of benzene over V_2O_5 [6] had a specific gravity of 1.106-1.137. 25-30% aqueous solutions of maleic acid were prepared from commercial maleic acid GOST 2806-51.

Benzoquinone was determined on a LP-5 laboratory potentiometer at 20-50°.

Experiment 1. 20.0 ml of the 40% production liquor of maleic acid, and 10 ml of 10% KI solution were taken. The liberated iodine was titrated from an automatic microburet with 0.1 N thiosulfate. The end point was established by the maximum $\Delta E/\Delta C$. The amount of benzoquinone was calculated on the basis that 1 ml of 0.1 N thiosulfate corresponds to 0.0054 g of benzoquinone.

The titration curve is shown in the diagram.

The end point was found at 8.24 ml which corresponds to 44.4 mg of benzoquinone.

Experiment 2. 20.0 ml of the same production liquor of maleic acid as that used in experiment No. 1 was taken; to this was added 76.2 mg of benzoquinone and 10 ml of 10% KI.

On titration a total of 119.0 mg of benzoquinone was found. The difference between the first and second titration, amounted to 74.6 mg i.e. to 98% of the theoretical value. Similar results were obtained on adding various other amounts of benzoquinone. Formaldehyde does not affect the results during benzoquinone determination.

The electrode potential is rapidly established and 3-5 minutes are taken to carry out a titration.

Temp., in °C	$Na_2S_2O_3$ used up, in ml	Benzoquinone found, mg	% recovery of benzoquinone
47	3.90	42.2	105.5
44—48	3.85	41.7	104.3
44—50	3.77	40.7	101.8
20	4.07	44.0	110.0

Results for the direct potentiometric titration of benzoquinone with thiosulfate are given in the Table.

For each test 40 mg of benzoquinone and 20.0 ml of a 25% aqueous soulution of maleic acid were taken.

In this case 1 ml of 0.1 N $Na_2S_2O_3$ corresponds to 0.0108 g of benzoquinone. The electrode potential was only established slowly under these conditions, independently of the rate of addition of $Na_2S_2O_3$ and of the temperature. Direct titration of benzoquinone for any particular case cannot therefore be recommended.

SUMMARY

A method which is suggested for the determination of benzoquinone in maleic acid solutions is based on potentiometric titration with thiosulfate of the free iodine liberated during the interaction of potassium iodide with benzoquinone in acid media. Formaldehyde does not interfere.

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* The production liquor of maleic acid was extracted with benzene, as a result of which benzoquinone was isolated and identified.

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"Methods of Organic Chemistry," (Houben-Weyl) Fourth Completely Revised Edition. Editor E. Muller Vol. I, Part I. General Laboratory Practice. G. Time Press, Stutgart, 1958, pp. 1048.

The first part of the first volume of "Methods of Organic Chemistry," (General Laboratory Practice) edited by E. Muller, and published in January 1958, is the fourth edition, considerably enlarged and revised, of the well-known reference work of Houben-Weyl (the third edition was issued more than 20 years ago) in which a number of authors have participated, including O. Bayer, H. Meerwein, and K. Ziegler. 16 volumes will be published in the course of four years. The reference book will be devoted to questions of general laboratory practice, methods of organic analysis (Volume II), methods of preparing and the reactions of various classes of organic compounds, with special reference to high-molecular-weight compounds and various natural materials.

Volume I/I consists of 29 chapters containing valuable information on various materials used in the laboratory, and on methods of separating materials. A bibliography covering the literature up to 1955-1956 is included at the end of each chapter. Individual chapters (Glass apparatus connections, Ceramic masses, Repair of apparatus, Distillation and fractionation, etc.) are mainly of interest to the organic chemist. Some chapters contain information valuable for chemists working in other fields, particularly for the analytical chemist. In the chapter on the various types of glass for example, the chemical stability and physical properties of various makes of glass are described (e.g. glass for glass electrodes, light filters, etc.). In the chapter on metals and their alloys, tables are included illustrating the behavior of the metals and alloys used in the laboratory toward numerous chemical materials.

Measuring cylinders, crystallizing basins, water distillation apparatus, watch glasses, weighing bottles, beakers, etc. made from methacrylic ester polymers, polystyrene, polyamide, polyethylene, etc. and which are used in laboratory practice are described. Of interest for the analytical chemist is the replacement in certain cases of expensive platinum by polychlorotrifluoroethylene; e.g. during removal of H_2F_2 in silicate analysis (180°) it is possible to carry out evaporation in basins made from polychlorotrifluoroethylene mounted in aluminum; H_2F_2 can be stored in polyethylene vessels. Vessels which are capable of standing up to even aqua regia can be made from polytetrafluoroethylene.

Separate chapters are devoted to decantation and filtration, washing, clarifying and decolorization of solutions, and breaking up of emulsions. Purification of organic materials by making use of the formation of complex salts with the heavy metals (for hydroxy-acids, the hydroxyquinones of α-amino acids, oximes, diketones, bases, sulfamide preparations) is described. The theory and practice of extraction and partition are described separately. In the chapter on ion exchange, the basic characteristics of certain cation-and anion-exchange resins are described, as well as those of some resins used for special purposes (for catalysis, decolorization, sorption of oxygen). The use of ion-exchange chromatography for the determination of total electrolyte content, and for the removal of PO_4^{3-}, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$ is described; the study of complex formation, the preparation of pure reagents (for example, by passing H_2O_2 cooled to 0° through Wofatite, the stability of the former can be increased), determination of Cl^- in NaOH, preparation of standard NaOH solution by starting from NaCl and an anion-exchange resin in the OH^- form are also discussed.

A special chapter is devoted to redox resins, which are acquiring increasing importance.

The apparatus and application of dialysis, electrodialysis, and electrophoresis are considered.

The conditions required for drying materials are described. Volume I/I concludes with a discussion of the planning and construction of a laboratory for organic chemistry.

On the whole this reference book is fairly complete, and the experimental techniques current in modern laboratories are fully discussed; theoretical questions are also included. Many of the chapters are of considerable interest to the analytical chemist.

V. G. Tiptsova

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EVALUATION OF THE RESULTS OF SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS BY MEANS OF POISSON'S DISTRIBUTION

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Evaluation of analytical results on the basis of errors calculated by some means or other, is only possible when the law governing the distribution of these errors is known. The errors of quantitative spectrographic analysis expressed in percentage concentration, or as the logarithms of the line intensity, usually conform to normal distribution [1-6]. In this case the square error is calculated. Using the law of normal distribution, and knowing the size of the error, it is easy to establish the probability of the appearance of experimental results with deviations not exceeding some given limit.

TABLE 1

Semi-Quantitative Determination of W

Range of error, in parts of σ	Absolute frequencies: Expected for a Gaussian distribution		Absolute frequencies: Actually found	
0,0 —0,67	72,4		80	
0,67—1,0	27,1		19	
1,0 —1,4	22,8		6	
1,4 —2,0	16,9		0	
2,0 —2,6	5,3	6,7	26	41
2,6 —3,0	1,0		12	
>3,0	0,4		3*	

c=0,01—0,05%.

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*Two errors had the value 9σ.

Evaluation of the accuracy of semi-quantitative spectrographic analysis is considerably more complicated; this analytical technique is very widely used in geological-prospecting work (metallometric surveys, preliminary sorting of geological test samples, etc.). Annually in the USSR several millions of such analyses are carried out by various geological-prospecting organizations.

The results of semi-quantitative spectrographic analysis are usually presented by means of a specially developed scale of discrete values. For example, when a test material contains 0.01% of some material, then according to a scale corresponding to a three-stage concentration range, the results can be represented by a series of discrete results: 0.01, 0.03, 0.1, 0.003, and 0.001% etc. The discrete nature of the analytical results, and the large error involved, which is comparable to the mean value of the analytical results, indicate that we cannot expect a normal distribution for the analytical results. As an example, in Table 1 a comparison is made of the experimentally established distribution of errors for the semi-quantitative analysis of tungsten, and the expected distribution based on a Gaussian distribution. It is quite obvious from Table 1 that there is not even an approximate agreement between the distribution actually observed and normal distribution. Calculations of the criteria of agreement gave, in this instance, the following results: $\chi^2 \approx 208$ for three degrees of freedom: P (> χ^2) 0.00001. Among 146 determinations there were two samples with errors of 9σ. These errors cannot be discarded as spurious, since they have also been observed during the determination of other elements, although their appearance would be excluded in practice, were the distribution of errors to conform to a normal distribution. A similar disagreement between the expected frequencies and those actually found has also been observed during the semi-quantitative determination of other elements.

The idea behind using one error or another for evaluating the experimental results is, that by using one cipher, the large amount of experimental material which has been obtained during the study of errors can be ciphered. Such a compilation of information can only be carried out when the law of the distribution of errors is known — this is the key by means of which this information can be interpreted in future. In the case under discussion — the semi-quantitative determination of tungsten and other elements — the distribution of errors is still unknown; accordingly, calculation of the square error is of no metrological significance. Knowing this value, it is impossible to forecast the frequency of the appearance of one particular deviation or another. It is doubtful in this case whether two square errors obtained in various laboratories characterize the quality of the work in these laboratories, since in such a case the factual material which is ciphered by these errors remains unknown.

A normal distribution might be expected according to the central limiting theorem of Liapunov, since the effect of a number of random factors distributed arbitrarily, under conditions where there are no factors which are greater than the majority of the remaining factors, is added up. In information theory, on the basis of the concept of entropy as a measure of the scattering of random values, it is shown that the normal distribution is the most random distribution of all possible distributions. In quantitative spectrographic analysis, analytical methods are usually developed so that the factors which determine the appearance of errors are excluded — by automatically fulfilling the requirements which are an outcome of the central limiting theorem of Liapunov — accordingly, a distribution approximating to a normal distribution is obtained [6]. A normal distribution, generally speaking, is a distribution of continuous values. Nevertheless, in practical work, all the results of measurements, including those of chemical determinations, are discrete to some extent or other, in the first instance because the results of measurements can only be obtained as a multiple of the smallest unit which the instrument used for measuring is capable of, and, secondly, in view of rounding off which is always adopted during calculation. During quantitative analysis, the extent of this discreteness is less than the observed changes in the value being measured, accordingly, one can with a fair degree of approximation ignore this factor, and regard x as a continuous value. The position is totally different in the case of semi-quantitative analysis: the coarse scale of evaluation has an essential effect on the distribution of the analytical results — this effect therefore becomes the dominating factor. In a random normal distribution the element of arbitrary randomness is introduced — the distribution of values becomes essentially discrete. As a result of this, the conditions for the appearance of a normal distribution, which is a consequence of the Liapunov theorem, are destroyed. In this case, on the basis of formal mathematical considerations, we might expect a Poisson distribution, which may be regarded as a special limiting case of a normal distribution [7], on which is superimposed the limitation indicated above imposed by the use of a coarse measuring scale which quantizes the experimental results.

Let us consider the following case. During styloscopic analysis, the elements are determined by comparing the intensity of two analytical lines. Here, we are dealing with a coarse measuring scale, which is determined by the number of pairs of lines with equal intensity in a given concentration range, since the human eye can only contrast the equality of two intensities. If the styloscope should be provided with a special photometric setup by means of which the line intensity can be changed uniformly, then we would get a fairly fine measuring scale, by means of which it would be possible to change over from discrete semi-quantitative analysis to continuous quantitative analysis.

Thus, on the basis of general metrological considerations, it is possible to give the following fairly strict classification of analytical methods:

1) Quantitative analysis — this is a method in which the results of repeated, successive determinations of the same value form a practically continuous collection of values. The degree of discreteness which is introduced by the measuring scale of the apparatus, rounding off during calculation, etc., is not the dominating factor in the general balance of errors. The values of the errors differ by one order or more from the content being determined.

2) Semi-quantitative Analysis — this is a method in which the results of repeated, successive determinations form a discrete succession of values, while the degree of discreteness (the value of the interval between two possible determinations) is of the same order of magnitude as the value being determined.

3) Qualitative Analysis — this is a special case of semi-quantitative analysis, where the results of a determinatio are mutually exclusive: the element is either present or not.

In order to present the results of semi-quantitative analysis in the form of a Poisson distribution, we shall use a special code consisting of a series of whole, positive numbers: 0, 1, 2, 3 . . . Let us assume that we have a

TABLE 2

Semi-Quantitative Determination of W, Mo, Sb, Cu, Bi, Zn, Pb, and Ag

	Absolute frequencies															
	W 0.01–0.03%		Mo 0.003–0.01%		Sb 0.01–0.10%		Cu 0.03–1.00%		Bi 0.003–0.01%		Zn 0.03–0.50%		Pb 0.01–0.50%		Ag 0.001–0.003	
	Expected acc. to the Poisson distr.	Actually found experi-mentally	Expected acc. to the Poisson distr.	Actually found ex-periment-ally	Expected acc. to the Poisson distr.	Actually found experi-mentally	Expected acc. to the Poisson distr.	Actually found experi-mentally	Expected acc. to the Poisson distr.	Actually found experi-mentally	Expected acc. to the Poisson distr.	Actually found experi-mentally	Expected acc. to the Poisson distr.	Actually found experi-mentally	Expected acc. to the Poisson distr.	Actually found experi-mentally
0	97,6	92	88,2	81	52,9	47	98,4	97	61,2	53	68,4	61	26,7	24	11,5	10
1	39,2	49	45,7	57	35,5	44	39,4	43	33,8	48	42,7	53	21,6	26	13,2	16
2	7,8	5	11,9	10	11,9	11	7,9	7	9,3	5	13,1	13	8,8	7	7,4	5
3	1,0	0	1,8	0	2,6	1	1,0	0	1,7	0	2,4	0	2,3	3	2,8	5
4	0,1	0	0,2	0	0,3	0	0,1	0	0,2	0	0,3	0	0,4	0	0,8	0
λ	0,40		0,52		0,67		0,39		0,55		0,62		0,81		1,14	
σ^2/λ	0,77		0,75		0,73		0,86		0,62		0,72		0,86		0,86	
$P(>\chi^2)$	~0,04		≃0,04		≃0,07		≃0,3		≃0,001		≃0,05		≃0,2		≃0.3	
$P(<\chi^2/(l-1))$	≃0,02		≃0,01		≃0,02		≃0,05		≃0,001		≃0,01		≃0,25		≃0,3	

sample containing 0.01% of some element or other, and that we carry out determinations using the threefold concentration scale. The following results might be obtained during repeated determinations: 1) c = 0.01%, in this case, the determination has been carried out without error and the results can be coded by the number 0; 2) c = = 0.03% or c = 0.003% – the experimental results fall into the nearest concentration range (to the right or left of the true content) and the error can be coded by the number 1; 3) c = 0.1% or c = 0.001% – the experimental results fall within the second concentration range, the error can be coded by the number 2, etc. For repeated determinations we would get a series of numbers:

$$0\,0\,2\,0\,1\,0\,2\,3\,0\,0\,0\,1\,0\,2\ldots \tag{1}$$

One often comes up against the presentation of experimental material by means of a series of numbers (1) in applied problems in the theory of probability. Let us assume that in a certain region T there are N points. The question may arise: what is the probability of finding m points in region t which is part of T? In the same way, for example, it is possible to formulate the problem which arises during a study of the distribution of structural components on a macrosection by means of a measuring grid. In this case the results of measurements of the number of nodules of a certain structural component falling within one measuring cell or another, are expressed by a series of numbers. If the points in region T are distributed randomly and independently of each other, it can be shown that the Poisson distribution is fulfilled [8]:

$$P_{\lambda}(m) = \frac{\lambda^{m} e^{-\lambda}}{m!}, \tag{2}$$

where λ is the mean number of points in region t (the mean arithmetic series of numbers (1)); m = 0, 1, 2...., $P_{\lambda}(m)$ is the probability that m points fall within the region t being measured. If the Poisson distribution is strictly observed, it is easy to show that $\sigma^2 = \lambda$.

In semi-quantitative analysis the multitude of determinations can be regarded as a continuous sequence of equal intervals t, while to each determination there corresponds some number of a series (1) which characterizes one error or another of the determination.*

Poissson's law, generally speaking, is only fulfilled when the probability of the appearance of an event in the short interval Δt, is proportional to Δt, and events appear independently of each other [9]. The parameter of the Poisson distribution can be represented by the expression: $\lambda = kt$, where t is interpreted as some measure of the section in which the event appears; $k = N/T$ is the average number of events appearing in unit measure. In semi-quantitative analysis, the probability of the appearance of an error is inversely proportional to the chosen multiplicity of the concentration scale. Accordingly, in our case, the interval t should be regarded as some arbitrary measure, by means of which the concentration of the test material in the sample is expressed, and this measure can assume the values $^1/_3$, $^1/_2$, $^1/_{1.5}$ etc. according to whether 3, 2, or 1.5-fold intervals for the concentration scale are chosen for analysis. Poisson's law can be written in the form:

$$P_{kt}(m) = \frac{(kt)^{m} e^{-kt}}{m!}. \tag{3}$$

If in any series of experiments with a measure t_1 an accuracy of $\sigma^2 = \lambda$ is achieved, then using the relation $\lambda = kt$, it is possible to achieve accuracy for another measure t_2 (for a concentration scale with another multiplicity).

Table 2 contains results obtained by treating material obtained during a study of the accuracy of semi-quantitative spectrographic analysis of synthetic standards with known amounts of the test elements. The standards were prepared on the basis of the following compounds: 1) SiO_2; 2) $SiO_2 + CaCO_3$ in the ratio 1 : 1; 3) $SiO_2 + FeS_2$ 3 : 1; 4) $SiO_2 + CaCO_3 + MgO$ 3 : 2 : 1; 5) $SiO_2 + Na_2CO_3$ 3 : 1; 6) $SiO_2 + Al_2O_3$ 3 : 1; 7) $SiO_2 + CaCO_3 + MgO$ 4 : 1 : 1; 8) SiO_2 + pyrites 4 : 1. The analysis was carried out by blowing the test material with a stream of air between the carbon electrodes of an A.C. arc [10]. Each standard was analyzed 10-15 times, using a scale with $t = {}^1/_3$. The experimental error for samples differing in composition were combined in one collection of numbers of type (1). For example, when we had two standards with contents of 0.03 and 0.01%, and on analysis we found 0.03% in both cases, then, for the first sample this result was coded by the number 0, while the second was coded by the number 1, etc. Table 3 contains results obtained by treating 797 analyses of niobium in geological samples. For spectrograms taken on the same plate, determination was carried out both semi-quantitatively (using a scale with $t = {}^1/_2$), and quantitatively by using a microphotometer and a calibration curve. Comparison of the results obtained by both the methods indicated was carried out by means of a series of numbers similar to series (1).

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* In Poisson's distribution, m = 0, 1, 2, 3 . . . is an arithmetic progression, while in our case the concentration intervals increase in geometric progression. This circumstance should not lead to any perplexity, since the value actually measured ΔS is proportional to the logarithm of the concentration, while on a logarithmic scale we shall have an arithmetic progression.

TABLE 3

Semi-Quantitative Determination of Nb

m	Absolute frequencies	
	Expected from Poisson distr.	Actually found
0	424,5	399
1	267,4	309
2	84,4	74
3	17,7	14
4	2,8	1
5	0,4	0
λ	0,63	
σ^2/λ	0,86	
$P(>\chi^2)$	0,004	
$P(<\chi^2/(l-1))$	0,002	

It follows from an examination of the tabulated results that the frequency distribution of the results obtained experimentally is in fairly good agreement with the distribution to be expected from a Poisson distribution. It is interesting to note that the large errors ($m = 2$; $m = 3$) which are unavoidable during semi-quantitative determinations occur with frequencies which agree quite well with the frequencies expected from a Poisson distribution.

In order to make an absolutely objective evaluation of the probability of the deviation between experimental and calculated frequencies, criteria of agreement were calculated:

1) We determined the weighted sum of the squares.

$$\chi^2 = \sum_{i=1}^{s} \frac{(n_i' - n_i)^2}{n_i'}, \tag{4}$$

where $n_1 n_2 \ldots n_s$ is the experimental series of frequencies; $n'_1 n'_2 \ldots n'_s$ the theoretical series of frequencies calculated on the basis of (2) in which the value λ found for the experimental series is substituted; s is the number of frequencies in the series. The sum found (4) is distributed approximately like χ^2 with $s-2$ degrees of freedom when all the values $n'_i \geq 5$ (when certain groups do not satisfy this condition they are combined).

2) We determined the value [9]:

$$\chi^2 (l-1) \approx \frac{\sum_{i=1}^{l} (x_i - \lambda)^2}{(l-1)\lambda} = \frac{\sigma^2}{\lambda} \tag{5}$$

where $x_1 x_2 \ldots x_l$ is the series of values obtained by us corresponding to series (1). The distribution $\chi^2/(l-1)$ is tabulated in [11] right up to large values of $(l-1)$.

Results for the calculations* of the criteria of agreement are given in the lower columns of Tables 2 and 3. We see that in most cases $P(>\chi^2) \geq 0.04$, while in three cases this value is > 0.20; all this testifies to the accuracy of our hypothesis regarding the agreement between the experimental frequencies and Poisson's law. The ratio σ^2/λ proved to be always less than unity, this decrease being almost invariably within reasonable limits, since, in almost all cases, the probability $P(<\chi^2/(l-1)) \geq 0.01$, while in three cases it was even considerably greater than 0.05. In our case, naturally, one cannot count on such good agreement between experimental and theoretical results, as is possible, for example, during the study of electron emission from a cathode when additional non-random factors are completely excluded. In semi-quantitative spectrographic analysis, already in view of its limited sensitivity, in a number of cases there may occur non-random deviations between the experimental results and Poisson's law. For example, if we analyze a sample with a low content of test material, the appearance of a much higher result is by no means restricted, while the appearance of much lower results is restricted by the sensitivity limits of the method — all results below a certain limit will be expressed as "traces" , coding by one cipher. Accordingly, for samples with a low content of test material, the number of determinations with indices $m - 3$, $m - 4$ may be lower than what would be expected on the basis of a Poisson distribution — this circumstance lowers the value σ considerably; accordingly, in some cases, σ^2/λ will be appreciably less than unity.

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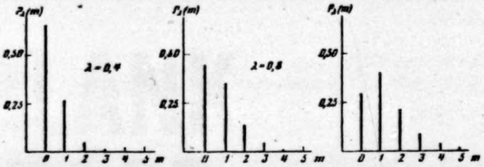
* All the calculations in Tables 1, 2, and 3 were rounded off considerably.

Thus, the errors of semi-quantitative spectrographic determinations, generally speaking, conform to a Poisson distribution,* although deviations from this law are possible in certain cases. In each case, we can affirm that the experimentally observed distribution of frequencies does not belong to any law which differs in principle from Poisson's law. As a measure for evaluating the accuracy of semi-quantitative determination it seems reasonable to use the value λ — the only parameter of the Poisson distribution. Knowing the value of λ, it should always be possible to find the expected distribution of the results of a determination by using equation (2), and thus evaluate the reliability of the results obtained. The form of the Poisson distribution depends on the value of λ. When $\lambda < 1$, then the first member (the member with $M = 0$) will be the greatest, and will be greater the smaller λ; when $1 < \lambda < 2$, then the second member will be a maximum ($m = 2$) — this is illustrated in the Fig. In the examples given by us, λ varies within the limits 0.4 to 1.14. The difference in the values of λ is amenable to a clear-cut physical interpretation. Thus, the fact that during determination of copper, we obtained a value of $\lambda = 0.40$, has its basis in the high concentration sensitivity of the Cu line Cu 2824.4 A on the basis of which the determination was made. This line is convenient for visual evaluation of concentration and is not subject to self-rotation in the working concentration range. This same is true of the line W 2896.4 A, which we used for determination of tungsten; in this case we obtained a value of 0.39 for λ. On the other hand, the silver line Ag 3280.7 A, according to which this element was determined, is self-rotatory early on, and is masked by the background; accordingly, it does not possess a high concentration sensitivity. In addition, the background interferes. As can be seen from Table 2, in this case $\lambda = 1.14$.



Graphs illustrating the occurrence of a discrete, random error conforming to Poisson's distribution.

When evaluating a method, naturally, in addition to the value of λ, it is also necessary to indicate the multiplicity of the scale of the concentration range, by means of which the determination was carried out and the limit of the sensitivity of the method, so that it is possible to take into account possible asymmetry within the given frequency group. If it should be necessary to compare the accuracy of methods, obtained for scales of different multiplicities, then, as indicated above, it should be possible to use the relation $\lambda = kt$. Thus, during determination of niobium (Table 3) on a two-fold scale ($t = \frac{1}{2}$) we get $\lambda = 0.6$; this permits one to assume that for a three-fold scale ($t = \frac{1}{3}$) we should have $\lambda = 0.4$.

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* It is necessary to point out that a Poisson distribution will only hold for a completely determined method of coding the errors, chosen so that conditions are obeyed which are essential for the discrete, random values to conform to Poisson's law. If the coding system suggested above is changed, the Poisson distribution may not be fulfilled. For example, if the series of numbers 0, 1, 2, 3, . . are used, not for coding the analytical errors, but for coding the analytical results so that the content of a test material below a certain limit is coded as zero, the first result determined by unity, the second by two etc. then, during successive repeated analyses of the same sample, we shall again obtain a series of discrete values, but in this case, the distribution will not be a Poisson distribution. Here the discrete values cannot be regarded as random events connected with some interval t, such that the possibility of the occurence of an event in the small interval Δt will be proportional to Δt.

In conclusion we shall consider some concrete examples of the characteristics of the method suggested in this article for evaluating experimental errors. Let us assume that a determination is carried out on a two-fold concentration scale, and that for a sample containing 0.2%, we have obtained two results 0.4 and 0.01%. From the point of view of normal evaluation of errors, we would obtain an error of 100% in both cases, and should expect the occurrence of these errors with equal probability. On the basis of the method we have suggested above, we would code the first result by the number m = 1, while the second results would be coded m = 4, and the probabilities of the occurrence of these results should be essentially different. Available experimental data indisputably confirm this last position. From the viewpoint of geologists using the results of semi-quantitative determinations, these two results are also essentially different. In the first instance the experimental result and the reliably established content of the test material in the sample are of the same order while in the second case the experimental result differs from the reliably established value by more than one order – this could lead to considerable misunderstanding when use is made of the experimental results. As a second example let us consider the following: during the determination of a component present to the extent of 0.01%, two results were obtained,0.001 and 0.1%. The first method of calculation gives, in the first instance an error of 90%, while in the second instance the error is 900% – we are dealing with errors of different order. When calculations are made on the basis of the method suggested in this article, in both cases the deviations would be coded by the same number – the probability of the occurrence of these errors is the same – such a result would be more natural for semi-quantitative determinations.

Considerations analogous to those adduced here show that during qualitative determination, one might expect the occurence of a binomial distribution. It has been shown in [12] that the error involved during the determination of the percentage of cementite in a micro-section can be evaluated by means of a binomial distribution, if this value is evaluated by means of a large number of successive qualitative determinations, where the observer randomly touches the micro-section with a sharp point, and notes whether or not the point falls on a grain of cementite or on a part of the micro-section surface which is free from cementite. Thus we get the following scheme for the application of distribution to analytical errors: for quantitative determination – normal distribution; for semi-quantitative determination – Poisson distribution; and for qualitative determination – binomial distribution.

SUMMARY

Semi-quantitative spectrographic analysis is widely used in geological prospecting, the results usually being presented by means of a specially developed scale of discrete values. It has been shown that the distribution of the errors for the determinations is essentially different from the normal one, and can be presented with a certain degree of approximation by the Poisson distribution.

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THE USE OF RADIOACTIVE ISOTOPES FOR STUDYING THE SPATIAL DISTRIBUTION OF ELEMENTS IN THE PLASMA OF A D.C. ARC DURING THE SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN URANIUM

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In a previous communication [1] we considered some of the methods of using radioactive isotopes for studying the processes of evaporation and excitation of the elements in various sources, during spectrographic analysis. In particular, attention was given to the possibility of using them for studying the spatial distribution of elements in arc plasma. The present article is devoted to the first results of these investigations. They provide new material for coming to a decision regarding the role of the "carrier", which, according to the suggestion of Scribner and Mullin [2] is often used for increasing the sensitivity of the spectrographic determination of a number of elements.

The study of the nature of the distribution of the atoms of various elements in the space of a d.c. arc was carried out by photographing the inter-electrode gap of the source in the gamma-rays of the radioactive isotopes of the test elements. The latter were introduced into uranoso-uranic oxide in the form of oxide powders or as solutions of their nitrates, (with subsequent calcining and then grinding the base in a mortar); after evaporation together with the atoms of the appropriate impurities, they were distributed according to some law or other in the inter-electrode space of the source. The distribution of the elements in the arc plasma was registered on a photographic plate in the gamma-rays of the isotope by means of a camera-obscura. At the same time, in order to study the distribution of the excited atoms of the same elements in the arc space, the inter-electrode gap was photographed through an interference filter. Comparison of the photographs of the arc taken simultaneously in gamma- and monochromatic rays emitted by the atoms or ions of the element, made it possible to draw some conclusions regarding the changes in the intensity of their emission in various regions of the arc plasma, and the law of temperature distribution. When the photographs were taken through the light filter, the optical system was controlled by a diaphragm so that the time required for obtaining satisfactory photographs of the arc in the rays of the element and in the gamma-rays was the same.

All the chemical operations connected with preparing the standards and samples, as well as the loading of the electrodes were carried out in a protective chamber by means of manipulators. The arc with radioactive isotopes (total activity about 400-600 m. Curies) was placed in a lead camera-obscura, prepared in the form of a cabinet and provided with protective devices and manipulators, which made it possible to change the electrodes at a safe distance, and made it possible for the research worker at a window to control the arc holder. Observation of the operation of the system was made with the aid of a periscopic system. A container with electrodes which had been prepared for the tests were placed in the camera-cabinet before commencing a test.

In order to prevent the ventilation system of the laboratory from becoming contaminated with radioactive dust from the material evaporating in the arc, the air sucked from the camera was passed through a protective filter. The general appearance of the experimental setup is shown schematically in Fig. 1. The casette with the photographic film for registering the image of the arc in the gamma-rays was placed in a box outside the camera-obsura, and was only subjected to radiation from the rays passing from the outlet opening of the camera. The optimum ratios between the dimension of the outlet opening of the camera-obscura and its distance from the films were chosen experimentally: diameter of the opening about 1 mm; distance – 100 mm; value of the inter-electrode gap 4 mm. Under these conditions, when working with samples with the activity indicated above, fairly intense and clearly-defined images of the arc were obtained, when the radiation was allowed to fall on the film for 18-20 minutes. The time for which an element is found in the arc plasma, obviously, depends on its volatility. Accordingly, the time during which readily volatile elements are found in the arc space is short, and is no longer than a few minutes; in choosing the specific activity of the radioisotopes it was essential in order to obtain sufficiently intense photographs, to photograph several samples in succession on the same place on the film. Under these conditions, in order to avoid distortion of the true picture of the distribution of the elements in the arc plasma, it was necessary to adopt special measures in order to maintain a constant distance between the electrodes in series of successive experiments. A large part of the photographs obtained in the course of the work described here for the distribution of various elements in the source plasma (Fig. 2) only gives an idea of the mean distribution of elements during the time of exposure.

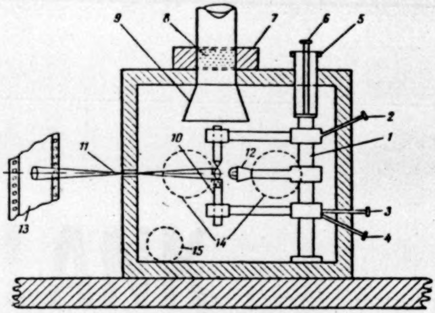

Fig. 1. Schematic features of the setup:
1) Arc holder; 2, 3, 4) handles for controlling the instruments used for adjusting the horizontal displacements of the upper and lower electrodes; 5, 6) handle for separate vertical control of the electrode displacements; 7) protective lead ring filter; 8) protective filter in the ventilation system; 9) funnel-shaped opening; 10) arc electrodes; 11) opening of the camera-obscure; 12) lamp for accurate setting of the electrodes on the optical axis by shadow projection; 13) film (casette not shown); 14) openings for manipulators and for changing the electrodes; 15) openings for loading the camera with containers containing electrodes.

For carrying out quantitative photometric measurements on the photographs, and for constructing curves showing the spatial distribution of the elements in the plasma of a D.C. arc, sensitometric curves were obtained for the photographic materials used for the gamma-rays. Blackening marks were projected on each of the films from a point source of gamma-rays by exposing various parts of the film at varying distances (r) of the photographic plates from the radiation source. Sensitometric curves were drawn within the coordinates S = f(Log r).

Curves for the spatial distribution of a large number of elements in the arc plasma were obtained. In Fig. 3, for example, are shown the most typical of them; these relate to elements possessing different volatilities (Sb, Ca, and Ta) and different ionization potentials. It is evident that the volatility of an element at the temperature established in the plasma of a D.C. arc, under the experimental conditions used, has a decisive influence on the shape of the distribution curves. On the curve for the spatial distribution of sodium (Fig. 3d) there is clearly shown the effect of the concentration of the sodium ions near the cathode in the d.c. arc; naturally this is not observed during work with an a.c. arc (Fig. 9b). The shape of the distribution curve for a given element, and the position of its characteristic points, are reproduced quite well from test to test.

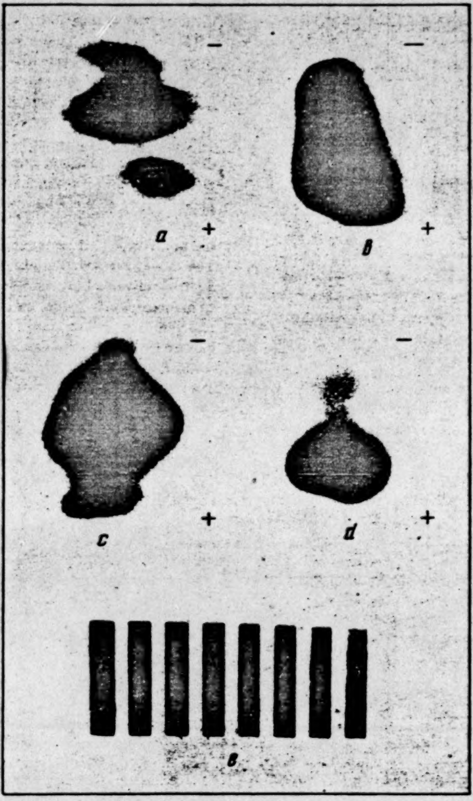

Fig. 2. Photographs taken in the gamma-rays of the radioactive isotopes Zn^{65}, Na^{24}, Ga^{72}, and Co^{60} which are characteristic of these elements in the plasma of a d.c. arc during their evaporation from uranoso-uranic oxide (I = 8 amperes); a) for sodium; b) for cobalt; c) for gallium; d) for zinc; e) blackening marks.

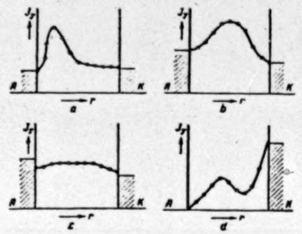

Fig. 3. Typical curves for the spatial distribution of various elements in the interelectrode gap of a d.c. arc during evaporation of impurities from uranoso-uranic oxide: a) for antimony; b) for gallium; c) for tantalum; d) for sodium; A – anode; C – cathode.

Of considerable interest was the study of the effect of a "carrier" on the nature of the distribution of atoms of impurities during their evaporation from uranoso-uranic oxide. As is known, the mechanism governing the increase in sensitivity of spectrographic determination of impurities in the presence of a "carrier" (e.g., Ga_2O_3 or AgCl), has not yet been explained, while the hypothesis advanced by the authors of the method [2] to explain the action of a "carrier", has, apparently, not received experimental confirmation [3]. One's attention is also drawn to the contradictory results obtained by various authors who have made a study of the effectiveness of this technique for enhancing the sensitivity of spectrographic analysis during the analysis of various materials under differing conditions. The curves shown in Fig. 4 illustrate the effect of the addition of various amounts of carrier (Ga_2O_3) to test sample of uranoso-uranic oxide, on the nature of the distribution of an impurity – antimony (about 0.05%) – in the interelectrode space of the source. As is evident from Fig. 4, while the distribution curves for antimony in the plasma differ sharply from the corresponding curves for gallium at relatively low contents of the "carrier" in the test samples, at gallium oxide contents greater than 1%, the curves for antimony completely duplicate the curve for the spatial distribution of gallium in the arc plasma.

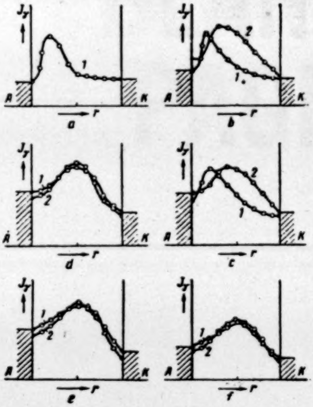

Fig. 4. Curves for the spatial distribution of antimony (1) and gallium (2) in samples with varying contents of "carrier" (gallium oxide): a) in the absence of any carrier in the sample; b) Ga_2O_3, 0.1%; c) Ga_2O_3, 0.5%; d) Ga_2O_3, 1%; e) Ga_2O_3, 2%; f) Ga_2O_3, 3%.

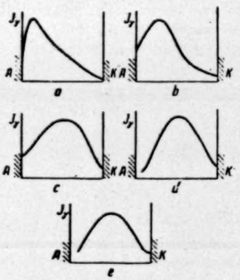

Fig. 5. Change in the spatial distribution curves for antimony with time, during its evaporation from a sample of uranoso-uranic oxide containing 2% Ga_2O_3 and 1% Sb_2O_3: a) 10 seconds after the arc has started to burn; b) 15 seconds after; c) 20 seconds after; d) 25 seconds after; e) 30 seconds after.

The curves in Fig. 5 illustrate the development of this process with time, the example taken in the case being one which contains 2% of gallium oxide and 1% antimony oxide.

As is evident from Fig. 5, in the course of the first 20 seconds (Curves a, b) there is observed a gradual transition from an asymmetric spatial distribution curve, which is characteristic of antimony atoms free from gallium,

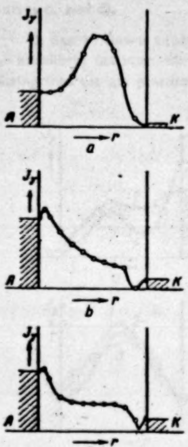

Fig. 6. Curves for the spatial distribution of silver during its evaporation from uranoso-uranic oxide; the silver was present as AgCl (a), Ag_2O (b), and metal (c).

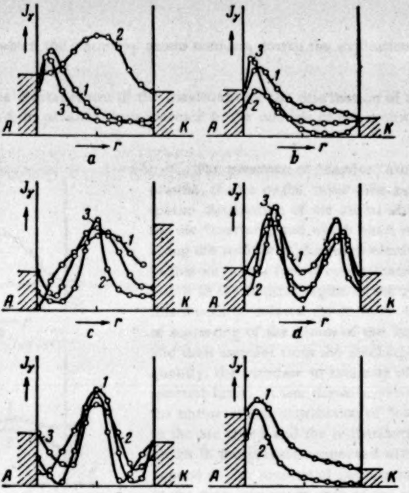

Fig. 7. Spatial distribution of antimony (1), gallium (2), and copper (3) when present together in uranoso-uranic oxide in various proportions: a) curves for antimony, gallium, and copper during the evaporation of each of them taken separately; b) Sb_2O_3, 0.1%; CuO 1%; Ga_2O_3 0.1%; c) Sb_2O_3 0.1%; CuO 1%; Ga_2O_3 2%; d) Sb_2O_3 0.1%; Ga_2O_3 2%; CuO 2%; e) Sb_2O_3 0.1%; Ga_2O_3 30%; CuO 10%; f) Sb_2O_3 10%; Ga_2O_3 2%.

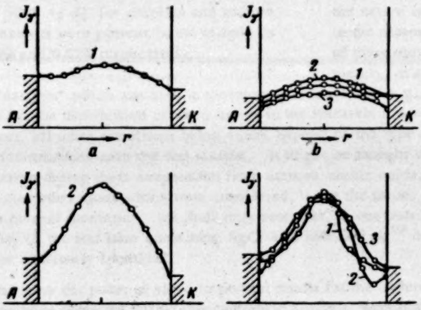

Fig. 8. Effect of calcium and gallium on the distribution curves of sodium in a d.c. arc. Curves (a) and (c) for calcium and gallium alone. Curves 1, 2, and 3 (b) and (d) relate to calcium, gallium, and sodium respectively.

to a symmetrical "gallium" distribution, to which the antimony atoms conform during the expiration of this time (curves c, and d).

It can be shown experimentally that the displacement of the maximum for the distribution of antimony to the middle of the inter-electrode gap proceeds in parallel to an increase in the content of the atoms of gallium passing into the arc plasma.

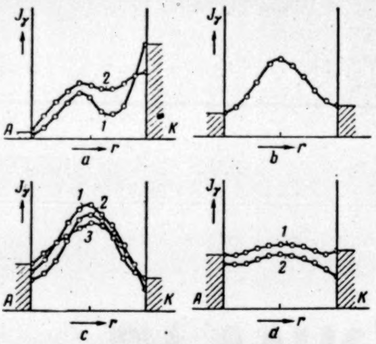

Fig. 9. Spatial distribution of sodium, calcium, and gallium during their evaporation from uranoso-uranic oxide containing varying amounts of these elements: a) fro sodium (1) using gamma-rays, in the absence of the other two impurities, and using a d.c. arc. Curve (2) was obtained using the line 5688 Al; b) for sodium, using gamma-rays in an A. C. arc; c) for gallium (1) and sodium (2) when present in the sample in amounts of 2% and 0.01% repsectively. Curve (3) for sodium was obtained using the line 5688 A; d) for calcium and sodium when these elements were present in the sample in amounts of 10% and 0.01% respectively.

The presence of "carrier" atoms in the arc plasma, thanks to the dome-like curve for the spatial distribution of the atoms which is characteristi for the "carrier", and which has a sharp maximum along the middle of the inter-electrode gap, leads, in this way, to a forced concentration of impurity atoms in the central region of the plasma. To this should be related the decrease in the extent of scattering of the atoms of the impurity elements, and their transfer from the discharge, and consequently, the increase in intensity of their characterist spectral lines. It was shown experimentally that the nature of the distribution of "carrier" atoms in the arc space and the redistribution of impurity atoms in the plasma connected with this, do not depend on the method of introducing the "carrier" in the inter-electrode gaps of the source. The simultaneous presence of "carrier" and impurity atoms in the test sample is not necessary for ensuring the redistribution mentioned above of impurity atoms in the arc space under the influence of carrier atoms. Evaporation of impurity and "carrier" (taken in an appropriate ratio to the impurity) into the plasma can be carried out separately also.

Examination of the results given in Fig. 6 leads one to think that the mechanism indicated above to explain the effect of gallium oxide on the nature of the distribution of impurity atoms in the plasma, and on the intensity of the lines of these elements, in the spectrum, could be completely, or at least partially, extended to cover the effect of other "carriers" which are used in spectrographic analysis; e.g., a carrier like AgCl. The same results show that the curves for the distribution of silver atoms in the inter-electrode gap, and the possibility of the occurrenc of this "carrier" effect, all other conditions being equal, depend on the type of compound used and the manner in which this element is introduced into the test sample. It might be thought that the state in which the silver atoms appear in the arc plasma during their evaporation from uranoso-uranic oxide, in which they were present as the chloride and in the two other cases which were considered, is not the same. This question is being treated in greater detail at the present moment. We shall only note that, as our tests have shown, the shape of the curves for decreasing activity of the test base containing AgCl with labelled Ag^{110} or Cl^{36}, depending on the time of arc burning[*] proved to be absolutely identical.

Interesting, and from our point of view, important results for the understanding of the role of the "carrier" and some other phenomena observed during spectrographic analysis, were obtained in the course of a study of the spatial distribution of impurities during their evaporation from uranoso-uranic oxide, containing, in addition to "carrier", large amounts of other elements, e.g., calcium and copper, whose atoms are distributed in the arc space according to another law which is different from that governing distribution of gallium. Some of the results relating to these experiments are shown graphically in Figs. 7-9; they convincingly demonstrate the arbitrary nature of the concept of "carriers", and the close connection between the results of the "carrier" effect on the spatial distribution of atoms of the impurity in the plasma of a d.c. arc, and the presence and relative content of other elements in the test sample. In the presence of two macro-components, the atoms of which are distributed differently in the arc space, the impurities will follow the atoms of the component that is present in the greater amount in the test sample. A particularly good example of the effect of macro-components on the nature of the distribution of impurities, and of elements contained in the test sample in smaller amounts than the main components, are the curves relating to sodium (Figs. 9 a, c, d).

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[*] For the method of obtaining these curves, see [1, 4].

Comparison of the distribution curves for gallium permits one to observe a certain characteristic which is common to them, namely the relation between the width of the concentration zone of the elements in the space of a d.c. arc and the relative content of the elements in the test sample.*

Taking into account all that has been said above, the following basic conclusions can be drawn:

1. The spatial distribution of atoms of different species in the plasma of a d.c. arc (presumably, just as in other sources) is not the same. The nature of this distribution depends, in the first instance, on the volatility of the element (or that of its compounds) at the temperature established in the source under the experimental conditions used. In the case of elements with low ionization potentials, under favorable conditions, there occurs a concentration of the ions of the element in the region near the cathode, when a d.c. arc is used. The shape of the spatial distribtuion curve for an element is almost independent of its content in the test sample.

2. If the difficultly volatile base contains in addition to the test impurity, a large amount of another element (we shall call this the macro-element), the atoms of which are distributed in the inter-electrode space according to a law which differs from that governing the distribution of the impurity, then, starting at a certain content, the macro-component will dictate the distribution of the atoms of all the other elements in the source space. In the presence of two macro-components – the atoms of which are distributed differently in the arc space – the impurity-elements (without any regard for the law governing the spatial distribution of their own atoms in the source) will follow the atoms of the macro-component present in the greater amount in the test sample. When the relative amounts of the macro-components are similar to each other, the impurities will be attracted by each of them in equal measure.

3. The elements which are the components of compounds normally used in spectrographic analysis as "carriers", and which favor an increase in the sensitivity of such an analysis, are characterized by a symmetrical, dome-like, distribution of the atoms in the space of the arc, with a sharp maximum at the center. The nature of the distribution of the "carrier" atoms in the arc space is independent of the method adopted for introducing it into the inter-electrode gap. The increase in intensity of the analytical lines of the impurity elements which is sometimes observed under favorable conditions when a "carrier" is used, is in no way connected with changes in the rate at which these elements pass into the plasma; this rate, as we have shown experimentally, and as results already published have shown [3], remains unchanged. The "carrier" only affects the distribution of the impurities in the inter-electrode space of the source, and leads to their compulsory concentration in the central region of the plasma. A consequence of this is a decrease in the degree of scattering and the passage of the atoms of the impurities out of the discharge. Accordingly, the effect of the "carrier" on the intensity of the spectral lines is not selective in character. In certain cases, for example when the sample contains large amounts of elements whose atoms are distributed in the arc plasma more asymmetrically than the atoms of the "carrier", the effect of the "carrier" may be weakened considerably or liquidated completely.

4. Differences in the spatial distribution of the elements in the inter-electrode gap, and the effect on this distribution of the composition of the test materials, may be one of the important factors which determine the relationship between the results of spectrographic analysis and the bulk composition of the samples, and the presence in these samples of so-called "ternary components".

This factor, however, has not hitherto been taken into account sufficiently and should be specially and systematically studied in the future.

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* It should be pointed out that all the processes described occur before uranium vapors pass into the plasma. Accordingly, the distribution of uranium atoms in the arc has no effect on the distribution of the other elements considered.

SUMMARY

Radioactive tracers have been used experimentally for the first time for studying the longitudinal distribution of elements in the plasma of a d.c. arc. Active isotope distribution in the plasma was recorded in gamma-rays by means of a camera-obscura made of lead. The spatial distribution of atoms of various elements in the plasma of a d.c. arc has been shown to be different, and to depend on the volatility of the elements.

The reasons for the effect of the carrier on the sensitivity of spectrographic determination of impurities in uranium have been ascertained. A symmetrical dome-like distribution of the atoms in the arc space, with a sharp maximum in the center is characteristic of the carrier, irrespective of the method by which the carrier is introduced into the arc gap.

The carrier only affects the distribution of the elements in the inter-electrode gap of the source, and leads to a compulsory concentration of the impurities in the central region of the plasma in accordance with the distribution of the carrier.

The effect of the carrier is not selective in character. It may be considerably reduced when large amounts of elements with a spatial distribution differing from that of the carrier are present in the sample.

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*Original Russian pagination. See C. B. Translation.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TANTALUM, BORON, INDIUM, AND RHENIUM

N. S. Poluetkov, L. I. Kononenko, and R. S. Lauer

Extraction-photometric methods are those methods in which an element is determined on the basis of the color of its compounds in an organic solvent after extraction of an aqueous test solution to which the requisite reagent has been added.

Recently, methods have been suggested for the determination of a number of metals (Table 1) which were based on the photometric measurement of colored extracts containing the metal to be determined in the form of the salt of a complex halogen acid with a basic dye, the complex being of the form $A_n \cdot Me \cdot X_m$, where A is the organic dye; Me is the test metal; and X is the halogen.

TABLE 1

Determination of Elements by Photometric Measurements of an Extract Containing a Compound of a Halogen Acid and a Dye

Element	Halogen acid	Dye	Solvent
Gallium	$HGaCl_4$	Rhodamine C	Benzene [1]
Gold	$HAuCl_4$	Rhodamine C	Isopropyl ether [2]
Antimony	$HSbCl_6$	Rhodamine C	Benzene [3-4]
"	$HSbCl_6$	Methyl Violet	Benzene [5]
Thallium	$HTlCl_4$	Rhodamine C	Benzene [6]
"	$HTlCl_4$	Methyl Violet	Benzene [7]

The same dye is a reagent for a number of metals (Table 1) while the requisite selectivity is achieved by the choice of halogen, acidity of the solution, and other experimental conditions. In order to discover new extraction-photometric methods, it is important to take into account the parallelism which exists between the extractability of simple or complex halogen acids according to an oxonium mechanism [8] and in the form of salts with organic bases. All the complex chloro acids of the metals mentioned in Table 1, and which are extracted in the form of salts with organic dyes, are extracted by diethyl ether or some other oxygen-containing solvents. On the other hand, simple or complex acids of the elements extracted by an oxonium mechanism are also extracted by solvents not containing oxygen in the form of arsonium compounds (Table 2).

It may be assumed, therefore, that in the case of elements whose acids are extracted according to an oxonium mechanism, or in the form of salts of arsonium compounds, conditions may be selected so that these acids can be extracted in the form of salts with basic dyes. This permits one to determine along what lines search should be made for new extraction-photometric methods. It should be borne in mind, however, that acids which are only weakly extracted according to an oxonium mechanism may not be extracted with dyes. Thus, As^{III}, Sb^{III}, Ge^{IV}, Te^{IV}, and other materials, which are only weakly extracted by diethyl ether from hydrochloric acid solutions [14], are not extracted in the form of rhodamine salts under analogous conditions. This is connected, presumably, with the fact that the concentration of the rhodamine base is several times less than the concentration established by the main component — the solvent — during extraction according to an oxonium mechanism.

The correctness of the concepts outlined above can be illustrated taking as examples new methods for determining tantalum, boron, indium, and rhenium which are described below.

TABLE 2

Extractability of Certain Elements in the Form of Complex or Simple Acids According to an Oxonium Mechanism and in the Form of Arsonium Salts

Element	Anion extracted	Solvent for extraction according to an oxonium mechanism	Extraction in the form of arsonium salts	
			Arsonium compound	Solvent
Fe	$Fe(SCN)_6^{3-}$	Diethyl ether	Triphenylmethylarsonium	o-Dichlorobenzene [9]
Co	$Co(SCN)_4^{2-}$	Diethyl ether and amyl alcohol	Triphenylmethylarsonium	o-Dichlorobenzene [10]
Co	$Co(SCN)_4^{2-}$	"	Tetraphenylarsonium	Chloroform [11]
Re	ReO_4^-	Ketones [12]	Tetraphenylarsonium	Chloroform [13]

1. Determination of Tantalum

According to an oxonium mechanism, tantalum can be extracted in the form of a complex fluoro acid by means of ketones, with its simultaneous separation from titanium and niobium [15, 16]. We found that from solutions containing hydrofluoric acid, tantalum can also be extracted in the form of salts with organic dyes of the diphenyl- and triphenylmethane series, and diazine, triazine, and phthalein dyes (auramine, fuchsine, methyl violet, base bright green, rhodamine, etc.) the solvents used for extraction being benzene, diethyl ether, etc. Accordingly, it is possible to determine tantalum on the basis of the color of the extract, which may be yellow, red, green, etc., depending on the dye chosen. The reaction is characterized by high specificity – the reaction is not given by niobium and titanium, nor by a number of other metals; calcium and the rare-earths, however, depress the intensity of the color given by tantalum.

Using methyl violet as the dye, and benzene as solvent, it was found that the optimum value of the pH of the solution is 2.3; the concentrations of the dye and the hydrofluoric acid in the solution being extracted should be strictly defined. Extraction with benzene should be carried out immediately after addition of methyl violet; the benzene extracts should not be kept in contact for a long time with glass (before photometric determinations are carried out, the extracts may be kept in platinum or porcelain crucibles). Of the other elements, only boron gives a color similar to that of tantalum; nevertheless, boron can be removed by evaporation with hydrofluoric and sulfuric acids. Colored extracts are also given by the nitrate and iodide ions, as well as divalent mercury.

Under the conditions described below, about 80% of the tantalum present is removed after one extraction; this, however, does not reflect on the accuracy of its determination, when it is borne in mind that the percentage extraction of tantalum is the same during preparation of both the standards and the test solutions.

Determination of Tantalum in Ores. 0.1-4, 0-6.0% Ta_2O_5. 50 mg of the finely ground ore is treated in a platinum crucible by heating with 5 ml of hydrofluoric acid to which 5-6 drops of concentrated sulfuric acid has been added. The solution is evaporated to dryness on a sand bath, and the residue fused with 2 g of sodium pyrosulfate on a gas burner and heated until liberation of SO_3 ceases, without overheating the residue. The salt in the crucible is then extracted with 25 ml of 4% ammonium oxalate, and the solution transferred to a 100 ml beaker; the crucible walls are carefully washed with distilled water, taking care, however, that the volume in the beaker does not exceed 35-40 ml. The solution is heated to the boil, and then cooled to room temperature; it is finally transferred to a 50 ml standard flask and diluted to the mark with water. In order to remove suspended particles of calcium oxalate 10-20 ml of the solution is centrifuged for 10 minutes. Filtration instead of centrifuging is not suitable in this case because high results are obtained, presumably, as a result of leaching out of nitrate ions from the filter, and these ions give the same reaction as tantalum. 4 or 2 ml of the centrifugate is taken for the determination. If less than 4 ml is taken, the volume of the solution is made up to the requisite value by addition of blank solution. The colored benzene extract is obtained by adding 2 ml of water, 2 ml of hydrofluoric acid (1.5 N), 5 ml of benzene, and 2 ml of 0.1% aqueous methyl violet, to 4 ml of test solution contained in a separating funnel. After extraction, and after the layers have been allowed to separate, the benzene extract is centrifuged in a dry centrifuge tube for 20-30 seconds, and the optical density measured in an FEK-M photoelectric colorimeter, using a 3 mm cell, and a yellow filter; the reference solution is benzene. The filter is a combination of a green light filter, provided with the apparatus, and an orange glass, and has a maximum transmission at about 580 mμ. A calibration curve is constructed for 10, 25, 50, and 75 γ of Ta (Fig. 1). A standard stock solution is first prepared containing 250 γ Ta/ ml, by dissolving 25 mg of the metal or the corresponding amount of tantalum pentoxide in 3-5 ml of hydrofluoric acid to which has been added nitric acid (2 drops of the concentrated acid). The solution is evaporated to dryness and the residue fused with 4 g of sodium pyrosulfate until sulfuric acid ceases to be evolved. The melt obtained is leached with 50 ml of 4% ammonium oxalate solution, this extract is boiled and then cooled, and finally diluted to the mark in a standard 100 ml flask. From this stock solution a working solution with a concentration of 50 γ Ta/ ml is prepared by diluting 10 ml of the former to 50 ml with black solution. The latter is prepared by fusing 4 g of sodium pyrosulfate and dissolving the melt obtained in 50 ml of a 4% solution of ammonium oxalate; this solution is then diluted to 100 ml with water. When constructing the calibration curve, the standard solution of Ta is made up to 4 ml with this blank solution; extraction is then carried out as described above.

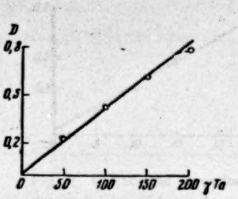

Fig. 1. Calibration curve for the determination of tantalum by means of methyl violet.

TABLE 3

Reproducibility of Replicate Determinations of Tantalum in Ores

Ta_2O_5 determined, in %		Mean	Deviation from the mean, in %
First determination	Second determination		
0.62	0.58	0.60	3.3
0.85	0.92	0.885	3.9
0.91	0.93	0.92	1.1
3.36	3.29	3.325	1.1
3.11	3.11	3.11	0
4.33	4.45	4.39	1.4
4.88	4.82	4.85	0.6
5.37	5.43	5.4	0.6
6.1	6.1	6.1	0

Table 3 illustrates the reproducibility of replicate determinations of tantalum in ores.

2. Determination of Boron

Boron can be extracted as the methyl-violet salt of hydrofluoric acid, just as in the case of the fluoro complex with tetraphenylarsonium. The latter was used for the preliminary separation of boron [17]. We chose the conditions for determination of small amounts of boron on the basis of this principle.

1-2 ml of the neutral test solution is placed in a platinum crucible and mixed with 0.5 ml of 2 N hydrofluoric acid and 0.1-0.2 ml of 20% sodium acetate solution; water is then added to bring the volume up to 3 ml, and the solution heated to the boil in order to get complete formation of fluoroborate. The solution is cooled and transferred to a quartz test tube; 3 ml of benzene is added followed by 0.5 ml of 0.2% methyl violet solution, and the whole shaken. The benzene layer, which is colored violet when boron is present, is poured into a centrifuge tube in which it is centrifuged for several minutes; the optical density of the centrifugate is measured on a FEK-M photocolorimeter using a 3 mm cell and a yellow filter. The relation between the value of the optical density and the amount of boron is linear up to 20 γ of boron (Fig. 2).

In Fig. 3 is shown the relationship between the intensity of the color obtained for 20 γ of boron and the amount of 0.2% methyl violet solution added.

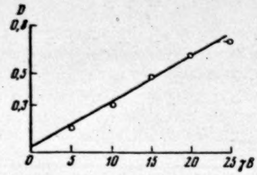

Fig. 2. Calibration curve for determination of boron by means of methyl violet.

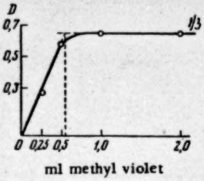

Fig. 3. Relation between the color intensity of the benzene layer and the amount of methyl violet solution added, when the amount of boron taken is 20 γ.

As the curve shows, the color becomes a constant at about 0.55 ml of methyl violet solution or 1.1 mg of the solid material. Thus, 20 γ of boron or $\frac{20 \cdot 10^{-6}}{10.8} = 1.85 \cdot 10^{-6}$ g-atom of boron corresponds to $\frac{1100 \cdot 10^{-6}}{556} = 1.97 \cdot 10^{-6}$ g.mole of dye (assuming that methyl violet is, mainly, the hydrochloride of pentamethylrosaniline $C_{24}H_{28}N_3Cl \cdot 9H_2O$). From this it fillows that 1 atom of boron corresponds to $\frac{1.97}{1.85} = 1.07$ molecules of methyl violet, so that the colored compound of boron has the formula (methyl violet) BF_4.

About 90% of the boron present is extracted during one extraction when the optimum conditions chosen are used, and the pH is 3.4 while the amount of boron taken is 20 γ. This incomplete extraction of boron does not, however, affect the accuracy of determination, as is evident from the following table — Table 4.

TABLE 4

Control Determination of Boron in Boric Acid Solution

Boron taken, in γ	Boron found, in γ	Difference, in γ
3.0	3.4	+0.4
8.0	8.4	+0.4
12.0	11.6	−0.4
14.0	14.0	0
18.0	17.2	−0.8

As for the selectivity of the reaction, what was said above of the reactions for tantalum is also true for boron.

3. Determination of Indium

Indium is extracted with diethyl ether from a medium of 3-5 N HBr as its ether compound with $HInBr_4$ [18]; in the same way, the compound of indium with a dye, for example, the bromoindiate of rhodamine C, is extracted with benzene.

The indium compound can be extracted from a medium of 1.3-4.2 N HBr with benzene; nevertheless, with increasing acidity, the color of the benzene layer becomes less intense. The color of a blank solution is stronger for lower values of the hydrogen bromide concentration; the optimum value for the intensity is obtained at a hydrogen bromide concentration of 2.5-2.8 N. As established experimentally in the course of experiments with radioactive indium, during extraction of 5 ml of an aqueous solution containing 0.5 ml of 0.5% aqueous rhodamine C solution by means of 5 ml of benzene, 28, 43, 34, and 24% of the indium present (50 γ) passed into the extract, when the HBr concentration was 1, 2, 3, and 4 N respectively.

The amount of indium extracted can, however, be increased to 95%, by adding acetone (1 ml) during the extraction; when this technique is used the color of the blank solution also increases. The optimum conditions were found to be: HBr concentration 2.5 N, amount of rhodamine C 1 ml of 0.25% solution, acetone 0.5 ml, volume of aqueous solution 10 ml and volume of benzene 25 ml; under these conditions, the optical density (from 0 to 1.1) at 530 mμ is directly proportional to the indium concentration — up to 50 γ of indium (the cell used was 5 mm and the photometer a Pulfrich photometer).

The reproducibility of the results obtained for determination of indium according to this method is shown in Table 5.

TABLE 5

Determination of Indium in Indium Chloride Solutions

In taken, in γ	In found, in γ	Difference, in γ	In taken, in γ	In found, in γ	Difference, in γ
6.3	6.0	−0.3	35.0	35.5	+0.5
7.5	8.0	+0.5	42.5	43.0	+0.5
18.8	18.5	−0.3	50.0	50.0	0
22.5	23.0	+0.5	72.5	72.0	−0.5

Of the other methods, a similar reaction is given by trivalent gold, molybdenum, tungsten, trivalent thallium, and iron, quadrivalent tellurium, and selenium, and divalent manganese. Divalent iron as well as Ca, Ga, Cr^{III}, Tl, Th, Bi, Be, Pb, As^{III}, U^{IV}, V^{V}, Ni, Co, Zr do not interfere. Trivalent iron can be reduced with ascorbic acid. 5 γ of indium can be determined in the presence of 10 mg Fe^{II} after addition of about 0.05 g of ascorbic acid to the solution prior to extraction.

During determination of indium in complex mixtures, it should be removed beforehand from the presence of interfering elements.

4. Determination of Rhenium

As mentioned already, rhenium, in the form of rhenic acid or its anion ReO_4^-, can be extracted both from acid and from alkaline solution by ketones [12]; this can be explained by the capacity of perrhenates to form oxonium compounds with ketones. Tests have shown that rhenium can be extracted with methylene blue, using ethyl acetate as the extractant; with methyl violet, using ethyl acetate as extractant, when extraction is carried out from ammoniacal and neutral media, and chloroform for extracting from a sulfuric medium; with auramine from sulfuric acid media, using chloroform and ethyl acetate as extractants; with rhodamine, using the same solvents from neutral solution, and ether from sulfuric acid media.

For quantitative determination of indium, extraction of the perrhenate of methyl violet with ethyl acetate from a neutral solution can be used. When the volumes of the aqueous and ethyl acetate phases are 5 ml, and the amount of methyl violet is 1 ml of a 0.1% aqueous solution, from 1 to 100 γ of Re can be determined by using a Pulfrich photometer and a 5 mm cell in conjunction with a filter which has maximum transmission at 610 mμ. The optical density is linearly related to the rhenium concentration (up to 100 γ Re). Although a number of anions interfere (such as nitrate, iodide, and bromide), the reaction has the advantage that it can be used for the determination of rhenium in the presence of molybdenum. The latter can be masked readily with tartrate; by carrying out the reaction in the presence of 0.2 ml of 40% Seignette salt, it is possible to determine 1 to 100 γ of rhenium in the presence of 20-70 mg of molybdenum trioxide.

TABLE 6

Control Determinations of Rhenium in a Mixture Containing 40 mg Molybdenum Trioxide

Re taken, in γ	Re found, in γ	Difference, in γ	Re taken, in γ	Re found, in γ	Difference, in γ
5.0	5.0	0	22.5	22.0	−0.5
12.5	12.8	+0.3	25.0	24.8	−0.2
15.0	14.4	−0.6	30.0	30.0	0
17.5	17.5	0	32.5	32.0	−0.5

Table 6 contains the results for control determinations of rhenium in the presence of 40 mg MoO_3, taken in the form of ammonium molybdate.

SUMMARY

Simple or complex acids of elements, which are readily extracted according to an oxonium mechanism, or in the form of salts with organic high-molecular weight bases, such as the arsonium compounds, can also, in many instances, be extracted in the form of their salts with basic dyes. On the basis of this fact, new extraction-photometric methods have been developed for the determination of tantalum, boron, indium, and rhenium.

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OXIDATION REACTIONS IN INTERNAL ELECTROLYSIS AND THEIR USE IN CHEMICAL ANALYSIS

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All the variants of the method of internal electrolysis proposed hitherto have been based on the deposition of the reduced element on an indifferent electrode [1-13]. Nevertheless, during internal electrolysis, it is possible to deposit the test element in an oxidized state on the indifferent electrode; for this purpose, the electrode which can be reduced (e.g. PbO_2), is connected with an indifferent electrode (e.g., a platinum electrode), and the electrode system formed immersed in a solution containing the test ion which is capable of being reduced. In this way thallium has been determined by deposition as Tl_2O_3 [14]. Ions of other metals, which are deposited on the anode during ordinary electrolysis [15] can also be determined by the method of internal electrolysis when a correct choice has been made of the oxidizing agent in the sleeve (catholyte). In the present article the possibility of such determinations is demonstrated. In the work described here the same setup as that used for the determination of thallium was used; the only difference was that a carbon electrode, provided with a means of attaching a platinum electrode to it, was immersed in the catholyte. The external appearance of the apparatus is shown in Fig. 1.

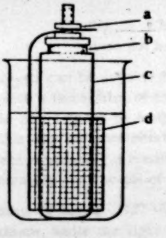

Fig. 1. Apparatus for carrying out internal electrolysis using an oxidation process on an indifferent electrode: a) screw; b) carbon electrode; c) sleeve containing oxidizing agent; d) platinum electrode.

Deposition of Manganese Dioxide* on the Anode

In order to establish the oxidation reaction: $Mn^{2+} + 2H_2O - 2e = MnO_2 + 4H^+$, it is essential to connect the sleeve of PbO_2 with the platinum electrode and immerse the whole in a solution of a divalent manganese salt. The galvanic element thus obtained $PbO_2 \| PbSO_4 / Mn^{2+} \| MnO_2(Pt)$ with short circuited electrodes will operate in the direction of the formation of manganese dioxide, since the normal oxidation potential of the pair: $PbO_2 + 4H^+ + SO_4^{2-} / PbSO_4 + 2H_2O$ ($E_h^0 = + 1.685$ volt) is considerably higher than the oxidation potential of $MnO_2 + 4H^+ / Mn^{2+} + 2H_2O$, which is equal to 1.28 volt.

The oxide of manganese $MnO_2 \cdot nH_2O$ which is deposited on the anode from a solution of $MnSO_4$ contains various amounts of water; the composition of the deposit depends to a very large extent on the rate of electrolysis. The higher the electrolysis rate, the higher the water content of the precipitate. During rapid deposition of manganese, the ratio $MnO_2 : H_2O$ in the deposit always differs on the platinum electrode. Nevertheless, when deposition of manganese is carried out slowly it is possible to get reproducible results; in this case, the composition of the precipitate which is deposited on the anode corresponds to the formula $MnO_2 \cdot H_2O$; the deposit answers the requirements of a gravimetric form.

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*Experiments on the anodic deposition of manganese were carried out in conjunction with B. Iordanov.

The composition of the precipitate obtained during anodic oxidation of Mn^{2+} may vary between $MnO_2 \cdot H_2O(H_2MnO_3)$ and $MnO_2 . 2H_2O(Mn/OH)_4$ or H_4MnO_4. When the pH of the anolyte is constant, the composition of the deposit should correspond to the formula $MnO_2 \cdot 2H_2O$, when the electrolysis is carried out with a high rate, and $MnO_2 \cdot H_2O$ when the rate approximates zero.

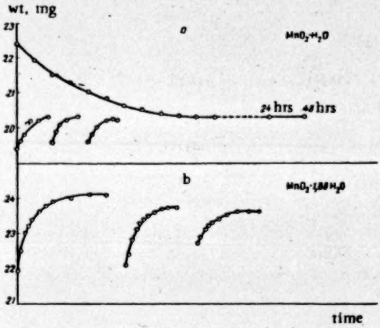

Fig. 2. Changes in the precipitate of $MnO_2 \cdot H_2O$ which does not have a stoichiometric composition, during drying.

Slow electrolysis can be achieved by observing the following conditions simultaneously: 1) the sleeve should be coated with a thick film of collodion; 2) the catholyte should be prepared from a mixture of PbO_2 and Na_2SO_4 in the ratio 20 : 1 (parts by weight) and moistened with 2 N H_2SO_4. The results obtained for determination of manganese in this way are considerably better than those obtained when a cathode is used (up to a certain limit, of course); this fact is probably a consequence of the sulfatization of PbO_2, as a result of which the total rate of electrolysis is decreased; 3) the pH of the anolyte should be kept at about 4.5.

The precipitate of $MnO_2 \cdot H_2O$ which is deposited on the anode is of a dark-brown color, and adheres quite firmly to the platinum, while the light-brown deposit whose composition corresponds to $MnO_2 \cdot 2H_2O$ (obtained during rapid hydrolysis) separates readily from the electrode.

The deposit formed during slow deposition, after washing in succession with distilled water, ethyl alcohol, and ether, weighs more than would be expected on theoretical grounds. Nevertheless, the weight of the precipitate decreases in air, and after approximately one hour its composition corresponds to the formula $MnO_2 \cdot H_2O$. The same phenomenon is observed when the deposit is left in a desiccator containing $CaCl_2$ for 20-30 minutes. After drying in the desiccator the weight of the deposit is always lower than would correspond to $MnO_2 \cdot H_2O$, but on standing in air the deposit absorbs water and acquires the expected weight. Loss and gain of water is a reversible process (Fig. 2a).

Manganese is determined as follows. A sleeve with a wall 2 mm thick is covered with a thick collodion film by immersing it 5-6 times in a 10% collodion solution. After immersion, the sleeve is left in the air for about 5 minutes, while after the last immersion it is left in the air for 15 minutes. The sleeve is preserved by filling it with a saturated solution of Na_2SO_4. When a sleeve filled with a mixture of PbO_2 and Na_2SO_4 in the ratio 20 : 1 is used, it is moistened with 2 N H_2SO_4; a thick carbon electrode is immersed in it, this electrode being provided with a nut and screw for fixing the platinum grid to it. The solution containing Mn^{2+} is poured into a 100 ml beaker and diluted to 30 ml with water; 3 ml of a saturated solution of CH_3COONH_4 is added followed by 0.5 g of NH_4NO_3 in order to increase the conductivity of the anolyte. Under these conditions a solution with a pH of about 4.5 is obtained; the pH remains almost constant during the whole duration of the electrolysis. The solution is then heated to 80° and the electrodes immersed in it. Heating is stopped and a slow stream of air passed through the anolyte. Electrolysis takes about 3 hours when about 15 mg of manganese is to be determined, while it takes about 5 hours for the determination of about 25 mg Mn. When electrolysis is complete, the platinum electrode is washed with water, ethanol, and ether; it is then placed in a desiccator containing $CaCl_2$ for 30 minutes, and then left in the air until the weight is constant.

The Table contains results obtained for the determination of manganese as $MnO_2 \cdot nH_2O$. The concentration of the $MnSO_4$ solution was established by precipitating the manganese as $MnNH_4PO_8$, and weighing as $Mn_2P_2O_7$. Electrolysis was carried out until a negative reaction was given for Mn^{2+} with $(NH_4)_2S_2O_8$.

TABLE

Mn taken in g	MnO_2 × × H_2O calc., in g	MnO_2 × × nH_2O found, in g	Mn calculated, in g	Relative error, in %	Duration of electrolysis, in hours
0,0078	0,0149	0,0149	0,0078	± 0,0	2,0
0,0078	0,0149	0,0149	0,0078	± 0,0	2,0
0,0087	0,0166	0,0167	0,0087	± 0,0	2,5
0,0106	0,0203	0,0276	0,0145	+36,8	0,5
0,0106	0,0203	0,0237	0,0124	+17,0	1,0
0,0106	0,0203	0,0201	0,0105	— 0,9	2,0
0,0106	0,0203	0,0203	0,0106	± 0,0	2,0
0,0106	0,0203	0,0205	0,0107	± 0,9	3,0
0,0157	0,0300	0,0300	0,0157	± 0,0	3,0
0,0157	0,0300	0,0301	0,0158	+ 0,6	3,0
0,0174	0,0332	0,0330	0,0173	— 0,6	3,5
0,0174	0,0332	0,0333	0,0174	± 0,0	3,5
0,0174	0,0332	0,0332	0,0174	± 0,0	4,0
0,0217	0,0415	0,0413	0,0216	— 0,5	5,5
0,0266	0,0508	0,0504	0,0264	— 0,7	5,0
0,0266	0,0508	0,0505	0,0264	— 0,7	5,5
0,0269	0,0513	0,0594	0,0311	+15,6	2,0

The tabulated data show that satisfactory results can be obtained for manganese by slow precipitation, when $MnO_2 \cdot H_2O$ is deposited on the electrode (correction factor 0.5234). The mean relative error is ± 0.7%. During rapid electrolysis, i.e., when a sleeve with only a thin covering of collodion is used and the pH of the anolyte is kept at > 4.5, the results obtained for manganese are not satisfactory. Qualitative detection of Mn^{2+} can be carried out under similar conditions.

Precipitation of mangenese dioxide on a platinum electrode is speeded up considerably by heating the solution to 60-70° and adding NH_4NO_3; the latter increases the conductivity of the electrolyte. Deposition of precipitate depends to a very large extent on the hydrogen ion concentration of the anolyte. The sensitivity of the reaction decreases considerably at pH's less than 4.0.

Mn^{2+} is identified as follows. The test solution is neutralized by means of dilute Na_2CO_3 solution to a weak acid reaction (in the presence of γ-dinitrophenol as indicator) and then heated to 60-70°. NH_4NO_3 is added to the solution and the setup for internal electrolysis with a catholyte of PbO_2 + dilute H_2SO_4 immersed in it. When Mn^{2+} is present a brown precipitate of $MnO_2 \cdot nH_2O$ will appear on the anode. When no deposit appears in the course of 15 minutes, it can be concluded that the solution does not contain Mn^{2+}. Using this technique, Mn^{2+} can be detected at a concentration of $0.8 \cdot 10^{-5}$ g Mn/ml in the presence of Ag^+, Al^{3+}, As^{5+}, Ba^{2+}, Be^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cs^+, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Na^+, NH_4^+, Ni^{2+}, Pb^{2+}, Rb^+, Sr^{2+}, Tl^{3+}, Ti^{4+}, UO_2^{2+}, Zn^{2+}, Zr^{4+}, MoO_4^{2-}, NO_3^-, SO_4^{2-}, VO_3^- and WO_4^{2-}. Small amounts of Cl^- ions do not interfere either.

Deposition of Lead Dioxide on the Anode

If a small excess of potassium or sodium hydroxide is added to a solution containing Pb^{2+}, and electrodes for carrying out internal electrolysis with a catholyte of $K_2S_2O_8 + H_2O$ (E_h^0 of the process: $S_2O_8^{2-} + 2e = 2SO_4^{2-}$ amounts to +2.05 volt) immersed in this solution of Pb^{2+}, then the reaction $PbO_2^{2-} - 2e = PbO_2$ will occur on the anode; as a result of this reaction a precipitate of lead dioxide will be formed on the platinum electrode. Sulfate ions which may penetrate into the anolyte do not interfere with deposition of lead dioxide, since the anolyte contains excess alkali in which $PbSO_4$ readily dissolves.

The brown deposit of lead dioxide may be formed not only by using the catholyte $K_2S_2O_8 + H_2O$, but also by using $NaBiO_3 + HNO_3$ ($E_h^0 > +1.8$ volt) etc. The deposit formed on the anode is very dense and adheres firmly to it.

At present, work is being carried out with the aim of improving the conditions for the quantitative determination of lead. These experiments show that the most suitable oxidizing agent for deposition of lead dioxide is $K_2S_2O_8$.

Deposition of the Hydroxide of Trivalent Nickel on the Anode

$K_2S_2O_8 + H_2O$ is placed in the sleeve. A precipitate of nickel trihydroxide is deposited on a platinum electrode from an ammoniacal solution of divalent nickel, because the oxidation potential of the pair $S_2O_8^{2-} + 2e = 2SO_4^{2-}$ is higher than the oxidation potential of the pair $Ni_2O_3 \cdot xH_2O + 6H^+/2Ni^{2+} + (x+3)\,H_2O$ ($E_h^0 = +\,1.75$ volt). Under these conditions the following process occurs on the anode: $2Ni^{2+} + (x+3)\,H_2O - 2e = Ni_2O_3 \cdot xH_2O + 6H^+$ since simple nickel ions form the complex ions $[Ni(NH_3)_6]^{2+}$. Simultaneously with deposition of nickel hydroxide on the anode, nickel hydroxide is also formed in solution, as a result of which the solution becomes turbid, and the bottom and the walls of the vessel in which electrolysis is carried out are covered with a film of deposit.

Similar experiments with a solution of a cobalt salt showed that the hydroxide of trivalent cobalt only deposits from solution at high Co^{2+} concentrations, and then only in insignificant amounts.

Deposition of Halogen Ions on the Anode

From tables of oxidation potentials [16] it is evident that the normal oxidation potentials of the system: $I_2/2I^-$ ($E_h^0 = +\,0.5345$ volt), $Br_2/2Br^-$ ($E_h^0 = +\,1.0652$ volt) and $Cl_2/2Cl^-$ ($E_h^0 = +\,1.3583$ volt) are lower than the value of the potential of the pair: $PbO_2 + 4H^+ + SO_4^{2-}\ PbSO_4 + 2H_2O$ ($E_h^0 = +\,1.685$ volt). Consequently, on immersion in a solution containing I^-, Br^- or Cl^- of a sleeve covered with a film of collodion and containing a catholyte consisting of PbO_2 + dilute H_2SO_4, the sleeve being connected to a platinum electrode, the following respective processes, will occur: $2I^- - 2e = I_2$, $2Br^- - 2e = Br_2$ and $2Cl^- - 2e = Cl_2$.

The capacity of I^-, Br^-, and Cl^- to be oxidized on an anode when the internal electrolysis method is used, can be applied for analytical purposes.

Since the potential of the oxidation reactions of I^-, Br^-, and Cl^- will differ appreciably from one another, one might expect that during continuous electrolysis, iodide ions will be oxidized first, they will be followed by the bromide ions, while the chloride ions come last. The iodine, bromine, and chlorine thereby liberated in succession can be readily detected by appropriate reactions.

During internal electrolysis such reactions as: $I_2 + 2H_2O - 2e = 2IO^- + 4H^+$ and $2\,IO^- + 4\,H_2O - 8e = 2IO + 8H^+$[*] may also occur. Furthermore, at high concentrations of Cl^- or Br^- and a low concentration of I^-, after oxidation of the latter, oxidation of Br^- and Cl^- starts immediately, which can also lead to incorrect results, since conditions are created such that I_2 can be oxidized to IO^- and even to IO_3^-: $I_2 + Cl_2 + 2H_2O = 2IO^- + 2IO^- + 2Cl^- + 4H^+$ and $I_2 + 5Cl_2 + 6H_2O = 2IO_3^- + 10Cl^- + 12H^+$. Nevertheless, all these difficulties which occur during detection of I^- at low concentrations in the presence of Br^- and Cl^- can be avoided, if the electrolysis process is interrupted from time to time.

When the solution contains I^-, then the blue color formed with starch during electrolysis does not permit one to distinguish the yellow color arising from bromine. But, if sufficient KCl is added to the solution, and, after detection of I^-, the electrolysis is carried out continuously, then the Cl_2 liberated will oxidize I_2 to IO^- or to IO_3^-, as a consequence of which the blue color of the solution disappears.

Detection of iodine and bromine ions in mixtures of I^-, Br^-, and Cl^- is carried out by observing the following conditions: 2 ml of solution is poured into a small beaker and 1-2 drops of starch solution added, followed by about 0.5 g of solid KCl. A sleeve containing PbO_2 + dilute H_2SO_4 and in contact with a platinum wire wound in a spiral around the sleeve is immersed in the solution. If the solution remains colorless, then the sleeve is immersed once again for a short time. When the solution contains I^-, then in order to detect Br^- it is necessary to carry out the electrolysis continuously until the solution is colorless, after which the yellow color given by bromine with starch appears.

The method permits determination of I^- at a limiting concentration of 1 : 100,000 and at ratios of I : Br equal to 1 : 10,000 and of I : Cl equal to 1 : 30,000 for amounts of $5.0 \cdot 10^{-5}$ g. Bromine ions can be detected at a limiting concentration of 1 : 40,000 and at a ratio of Br : Cl equal to 1 : 30,000, the amount being $5.0 \cdot 10^{-4}$ Small amounts of I^- and Br^- are detected almost immediately.

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[*] E_h^0 of the pair $2IO_3^- + 12H^+/I_2 + 6H_2O$ amounts to 1.195 volt.

Separate Oxidation of I^-, Br^-, and Cl^-

When internal electrolysis of a solution containing I^-, Br^-, and Cl^-, at the same time, is carried out using a galvanic element containing, for example, a ferric salt in the cathode compartment (E_h^0 of the pair: $Fe^{3+}/Fe^{2+} = +0.771$ volt) or Hg + H^+ (E_h^0 of the pair: $HgO + 2H^+/Hg + H_2O = +0.926$ volt) or Hg^{2+} (E_h^0 of the pair: $Hg^{2+}/Hg = +0.854$ volt) etc., then even when electrolysis is carried out continuously only oxidation of I^- will occur.

In the presence of KBr + KCl (and starch), and using a mixture of HgO + water in the cathode compartment, only oxidation of iodine ions occurs. The presence of bromide or chloride ions, not only does not interfere with the oxidation of I^- to I_2, but actually favors this oxidation, since the conductivity of the electrolyte increases considerably, and a blue color appears almost immediately.

Using a setup which consists of the galvanic element: $MnO_2 \| Mn^{2+}/2Br^- \| Br_2$ (Pt), it is possible, by continuous electrolysis of the solution, to oxidize Br^- without oxidizing the bromine liberated to BrO^- or BrO_3^-. The possibility of carrying out such an oxidation becomes understandable when one bears in mind that the potentials of the pair: $Cl_2/2Cl^-$, $HBrO + H^+/Br^- + H_2O$ and $BrO_3^- + 6H^+/Br^- + 3H_2O$, are respectively equal to: +1.3583 volt, + 1.35 volt, and + 1.44 volt.

Thus, during electrolysis of a solution containing I^-, Br^-, and Cl^- using a mixture of HgO and water in the cathode compartment, it is possible to oxidize I^- alone. A setup with a catholyte consisting of MnO_2 + dilute H_2SO_4 permits oxidation of I^- and Br^- but not Cl^-. Finally, using a mixture of PbO_2 + dilute H_2SO_4, it is possible to oxidize I^- as well as Br^- and Cl^-.

Using the galvanic element $HgO/Hg/2I^-/I_2$(Pt), iodide ions are readily detected in solutions containing down to $3.3 \cdot 10^{-5}$ g/ml iodine.

A very characteristic feature of oxidative internal electrolysis is the fact that by choosing the appropriate catholyte (oxidizing agent) it is possible to prepare a galvanic element – a setup for internal electrolysis – by means of which it is possible to carry out precisely the anode reaction required and to prevent the remaining oxidation processes. In this connection, oxidative internal electrolysis can be regarded as a method of electrolytic oxidation with control of the anode potential.

SUMMARY

It has been shown that by using the method of internal electrolysis it is possible to deposit on an anode made of an indifferent material, not only Tl_2O_3, but also the oxides of quadrivalent manganese and lead, trivalent nickel, and also to oxidize halide ions.

It has been established that it is possible to determine manganese quantitatively by precipitating it on the anode as $MnO_2 \cdot H_2O$. The average error is ± 0.7%. Methods are described for the identification of Mn^{2+}, and for detection of iodine and bromine ions in mixtures of I^-, Br^-, and Cl^-. Taking as an example the separate oxidation of I^-, Br^-, and Cl^-, it has been shown that oxidative internal electrolysis can be regarded as a method of electrolytic oxidation in which the anode potential is controlled.

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THE USE OF ULTRA-SOUND IN ANALYTICAL CHEMISTRY

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During recent years ultra-sound has been attracting the attention of research workers in the most diverse fields. In particular, ultra-acoustic methods are finding wide application in the practice of physico-chemical research; they are rapidly penetrating into the normal practice of physico-chemical scientific-research and production laboratories. Ultrasonic vibrations can cause oxidation and reduction, depolymerization, various molecular arrangements, "aging" of precipitates, depolymerization during electrolytic processes etc. Ultra-sound helps the study of the properties of materials and the laws governing various processes [1-7]. The setups necessary for generating ultra-sound have been described in the literature and are available to any laboratory.

The aim of the present article is to draw the attention of analytical chemists to the use of ultra-sonic methods, for solving theoretical and practical problems in analytical chemistry.

Of the greatest importance, in our opinion, for analytical chemistry, are the following properties of ultra-sound:

1. The relation between the velocity of sound in solutions and mixtures and the concentration of dissolved material, and the possibility arising from this of carrying out quantitative determination of compounds and individual elements.

2. The depolarizing effect of ultra-sound and the acceleration of the electrolytic deposition of the elements.

3. The effect of vibration (sounding) of gases under the action of an intermittent stream of thermal radiation, and the optical-acoustic method of analyzing gases and the method of studying absorption spectra in the infrared based on this.

4. The dispersing, coagulating, agitating action of ultra-sound; oxidation in an ultra-sonic field; the change in the rate of dissolution of materials, etc.

Of near-analytical importance is the application of ultra-sound for the determination of ion solvation; the use of the values of adiabatic compressibility, calculated from acoustic measurements, as "properties" in physico-chemical analysis, and the possibility of the identification of organic compounds.

The Relation Between the Velocity of Sound in Solutions and the Concentration of Dissolved Material [8-16]

It has been established that the rate of ultra-sonic vibrations in solution depends on the concentration of dissolved material, and, in certain cases, particularly for solutions of electrolytes, this relation is linear or almost linear. In Figs. 1 and 2 are shown curves relating the velocity of ultra-sound to the concentration of certain salts of uni- and divalent metals, and curves for aqueous solutions of some sugars. The relationship indicated above (linearity or near-linearity) is obeyed in both cases, as can readily be seen.

On the basis of assumptions regarding the additivity of internal energy in solution, Kudriavtsev [14] derived a formula relating the velocity of sound in the solution to the concentration of dissolved material, and to the velocity of sound in the pure solvent:

$$c^2 = (1 - \nu) c_0^2 + \nu \cdot 2{,}32 \cdot 10^7 \cdot \Phi_0,$$

where γ is the percentage by weight of the dissolved material in solution; c_0 is the velocity of sound in the solvent; Φ_0 is the energy of the ionic crystalline lattice of the dissolved material. The values for the velocity of ultra-sound in aqueous solutions of a number of halides and nitrates of the alkali metals, as calculated by this formula, are in good agreement with the experimental values.

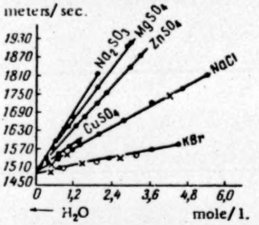

Fig. 1. Curves relating the velocity of ultra-sound and concentration of dissolved material for a number of salt solutions. Experimental values: o) P. Porozov; ×) A. Posynskii; o) E. Freier [9-11].

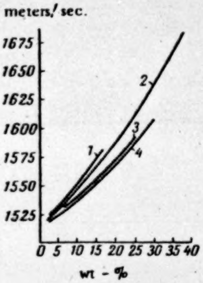

Fig. 2. Curves relating the velocity of ultra-sound and concentration of the dissolved material for aqueous solutions of some sugars: 1) D-fructose; 2) D-glucose; 3) raffinose; 4) saccharose [15].

As for mixtures of liquids: in the case of dissociating liquids, the velocity of ultra-sound is again linearly dependent upon the concentration, whereas in the case of non-dissociating liquids the relationship is often more complicated [16].

The existence of such a relationship means that it should be possible to carry out a quantitative determination of chemical compounds on the basis of measurements of the velocity of ultra-sound in solution; Sokolov [17] was the first to draw attention to this possibility. In order to carry out such a determination, Babikov [18, 19] used an impulse method for measuring the velocity of ultra-sound, and made an apparatus which enabled very small changes in this velocity to be measured. The basic components of an ultra-sonic impulse setup are: a generator of electric vibrations, a piezo-electric converter, a tube receiver, and an oscilloscope. Ultra-sonic impulses are generated by the quartz plate of the converter from electrical impulses, and, after passing through the test medium, are converted back again into electrical impulses. In Babikov's apparatus (USIS - apparatus for measuring the velocity of ultra-sound) ultra-sonic impulses following each other in a definite sequence are passed through the solution. These impulses are of very low intensity so as to exclude the possibility of the interaction of ultra-sound with the medium. When the concentration of the solution changes, there is a corresponding change in the velocity of ultra-sound, and there is a displacement of the impulses on the screen of the oscilloscope; the value of this displacement gives an indication of the change in concentration. Using a calibration curve constructed beforehand, it is easy to determine the amount of material in solution. The method possesses high accuracy and measurements can be carried out in a moving flow without taking samples. In this way the concentration of aqueous solutions of NaCl, the concentration of alcohol in water, and also the amount of methanol in ethanol have been determined. The error in the determination of alcohol is 0.1%.

Other methods such as the method of standing waves, the method of light diffraction in an ultra-sonic field, etc. [1, 20-22] can be used for the accurate measurement of the velocity of ultra-sound, as well as the impulse method. In all cases, however, the intensity of the ultra-sonic vibrations should be low enough to avoid their interaction with the medium.

We are speaking, really, therefore of a new method of physicochemical analysis. It is very desirable that there should be further studies in evaluating both the general possibilities and limitations of the method, and further studies on its practical use.

The Effect of Ultra-Sound on Electrolysis

Ultra-sonic vibrations of sufficiently high intensity lead to cavitation in a liquid medium — cavitation is a break up of the continuous medium, the spaces being filled with the vapors of the liquid and gases dissolved in the liquid. During the transition from rarefaction zones to compression zones, the cavitation bubbles begin to "swing" and during this process there occur local changes in pressure, temperature jumps, and electric discharges. Calculations show that the pressure may increase to several thousand atmospheres, while the temperature may rise to 2500° and higher. These phenomena lead to the activation of the oxygen and nitrogen dissolved in the water, while hydrogen peroxide, nitrous and nitric acids are formed. In addition to this cavitation effect, ultra-sonic vibrations at the same time lead to intensive agitation. This, presumably, accounts for the dispersion, coagulation, diffusion, crystallization, and dissolution which thereby occur.*

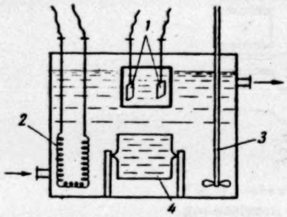

Fig. 3. Setup for studying electrodeposition by means of ultra-sound: 1) electrodes; 2) temperature regulator; 3) stirrer; 4) ultra-sound emitter.

The effect of ultra-sonic vibrations on electrochemical processes is very diverse [23]; it is expressed primarily in the depolarizing effect and in a decrease in deposition potential. Furthermore, "sounding" during electrolysis can lead to changes in the composition and character of electrolytic deposits, and can alter the duration of deposition, and the current yield etc.

By using ultra-sound, the hydrogen over-voltage on the cathode can be decreased to such an extent that it becomes possible to deposit aluminum and magnesium from aqueous solutions [24]. Irradiation with ultra-sound leads to a drop in the deposition potential of nickel, copper, and silver [25], and considerably cuts down the time required for the electro-deposition of copper [26] and lead [27]. For example, quantitative deposition of 0.3 g of lead takes only 20 minutes instead of one hour usually necessary for ordinary electrolysis. Work carried out by Kochergin and Terpilovsskii [28] on the effect of an ultra-sonic field on the electro-crystallization of metals, taking Cu, Ni, Co, Pb, and Sn as examples, has allowed several important conclusions to be drawn. It has been established that ultra-sonic treatment evens out the concentration of the ions at the electrodes to a considerable extent, decreases the value of the depolarization, degases the whole volume of the electrolyte, and favors the removal of bubbles of gas from the electrode surfaces, thereby permitting preparation of brighter and more dense deposits. The setup used is shown in Fig. 3. It has been shown in other papers [5] that the hardness of copper deposits obtained in an ultra-sonic field is 40% higher than that of deposits obtained under normal conditions. When the high-frequency vibrations are excited in the cathode mass itself, the metals deposited on such a cathode are of enhanced stability and possess better structures [29].

The effect of ultra-sound on the micro-structure of an electrolytic deposit may be twofold. On the one hand, the agitation effect and depolarization favor formation of deposits with crystals of large size, while the mechanical vibrations in themselves increase the number of centers of crystallization, and lead to the formation of fine-crystalline deposits [7].

Ultra-sound may prove useful during mass electrolytic determinations.

The Optico-Acoustic Effect and its Use

At the end of the last century it was established that gases and vapors which absorb the infrared, resonate on being subjected to the action of these rays, interrupted at the frequency of sound. During absorption of the radiation, the gas heats up and this leads to pressure changes. To the extent that the beam of infrared rays is interrupted the pressure becomes pulsating, i.e., sound develops. Veingerov studied this property in order to develop an optico-acoustic method of gas analysis, and to develop a method of studying the absorption spectra of materials in the infrared [30-36].

[*] The cavitation effect and the agitation effect can be considered in isolation; the agitation effect is itself connected with the formation of cavities. In some cases it is difficult to establish the decisive factor.

Elementary mono- and diatomic gases, O_2, N_2, and H_2, and the inert gases do not absorb the infrared; accordingly when air free from carbon dioxide and water-vapor is irradiated with the infrared no sound develops. When, therefore, a mixture of air and gaseous compound or compounds which vaporize, e.g., CO_2, is subjected to the action of an interrupted flow of radiation, the strength of the sound which develops will be proportional to the concentration of the absorbing impurity. The intensity of the sonic vibrations can be registered, for example, by means of a microphone and a galvanometer.

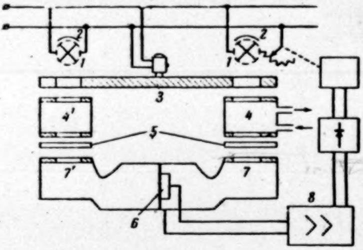

Fig. 4. Schematic diagram of M. L. Veingerov's gas-analyzer.

There are several types of gas-analyzers based on the optico-acoustic effect. The scheme of one of them is shown in Fig. 4 [37]. The infrared source is the emitter 1 provided with reflectors 2. The stream of radiation is interrupted by means of a rotating disc with opening 3. The test gas mixture passes continuously through the operating cell 4 into the reference cell 4' located in the second optical channel; this reference cell also contains a gaseous mixture with a known (e.g. zero) content of the test gas. After passing through the operating cell and filters 5, which only transmit a certain band of radiation, both sound beams pass into the cells of the differential ray-receiver 7 and 7'. Between these cells a microphone 6 is placed. When a change in concentration of the gas mixture occurs in the operating cell 4, there is a corresponding change in pressure in the ray-receiver 7; accordingly, the membrane of the microphone which experiences a difference in pressure from the sides of cells 7 and 7' will be set in vibratory motion. The alternating current which thereupon develops is registered by the galvanometer. Having calibrated the apparatus by means of mixtures with known contents of the test component, and having constructed the appropriate calibration curve, it is easy to determine an unknown concentration of the test component in a mixture.

In some cases it is possible to determine components in ternary mixtures. The method is applicable to the determination of gases which do not possess overlapping bands in their infrared absorption spectra, and also in those cases where acoustic measurements can be combined with chemical determinations of one of the components. In such cases it is advisable to use nomograms similar to those shown in Fig. 5 for the ternary mixture $He-O_2-N_2$.

Veingerov [36] has also shown the possibility of using optico-acoustic effect for studying the absorption spectra of gases and vapors in the infrared. If a known amount of gas or vapor which absorbs infrared rays is subjected to the action of a monochromatic beam of these rays, then the intensity of sound vibrations which thereupon develops will depend on the percentage absorption of the radiation of the given wave-length. By changing the wavelengths successively and registering the intensity of the sound vibrations continuously, it is possible to obtain the absorption spectrum of the material in the infrared.

The Use of the Oxidizing, Coagulating, and Other Properties of Ultra-Sound

Intensive ultra-sonic vibrations are widely used as a means of dispersing, coagulating, degassing, and mixing materials etc. Many of these effects are of considerable importance for analytical chemistry. Setups of different types, such as those described by Kuznetsov-Fetisov and Perpilovskii [38] can be used in practical work.

During a not very prolonged treatment with ultra-sound, many finely dispersed systems coagulate and can be readily filtered; for example, such treatment accelerates the sedimentation of barium sulfate [39]. In some instances it is possible to accelerate the clearing of various solutions by means of ultra-sonics. Thus, during precipitation of zinc with ammonium sulfide in an acid medium, about 24 hours are necessary for clarification of the solution. When, however, precipitation is carried out in a vessel subjected for 30 minutes to the action of ultra-sound, complete clarification is achieved within the hour [40].

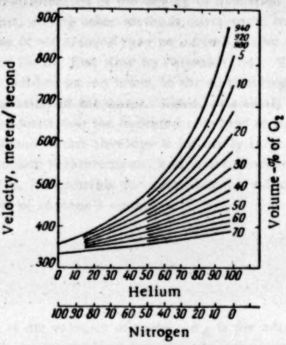

Fig. 5. Nomogram for the determination of the helium content in a mixture of He $-O_2-N_2$ saturated with water vapor Volume-%, O_2

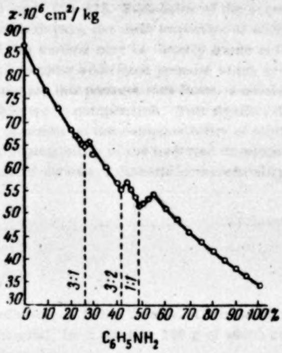

Fig. 6. Compressiblity isotherm (20°) of the system ethyl acetate – aniline.

There is little doubt that ultra-sound will find wide application in extraction processes, particularly during work with radioactive solutions, and in those cases when the use of continuous extraction is, for some reason, not expedient. It has been shown that extraction is particularly strongly accelerated when the ultra-sonic vibrations are directed at an angle to the direction of the movement of the extractant. Acceleration of extraction separation under the influence of ultra-sound is, presumably, related to a number of factors. Of importance in this connection is the increase in the area of the phase boundary as a result of emulsion formation, and the vibrations of the bubbles of extractant; the acceleration of diffusion in both liquids and the change of state of the boundary layer are also important factors [7].

Intense ultra-sonic vibrations modify the oxidation conditions in solutions [41-46]. It can be regarded as established that the oxidizing action of ultra-sound, just like the oxidation-reduction action of radioactive radiation, is secondary in origin; it is connected, as we have noted already, with the formation and subsequent "agitation" of the bubbles subjected to cavitation; changes in pressure, temperature and electrical phenomena are consequent upon this. The hydrogen peroxide, nitric acid and other oxidizing agents which are formed as the result of the activation of the hydrogen and nitrogen dissolved in the water also lead to oxidizing effects in an ultra-sonic field. Many examples of the oxidizing action of ultra-sound are known. During treatment with ultra-sound, sulfur is liberated from H_2S, while free iodine is liberated from potassium iodide solutions, and $FeSO_4$ is oxidized to $Fe_2(SO_4)_3$ etc.

The sensitivity and resolving power of photographic plates are known to be of great importance for spectrographic analysis. In this connection, therefore, the effect of ultra-sound on photographic emulsions is of interest. During treatment with ultra-sound, dispersion of silver bromide occurs. The decrease in particle size and the increase in homogeneity of the composition and concentration of silver bromide throughout the emulsion, permit one to prepare films with considerably greater sensitivity and resolving power [5, 47].

It should also be noted that ultra-sound has also been used for accelerating dissolution and for increasing the rate of heterogeneous reactions. Taking potassium ferrocyanide as an example, it has been shown that the rate at which this compound dissolves increases under the influence of ultra-sonic vibrations (even when compared with intensive mechanical agitation) [40]. Ultra-sonic radiation eliminates the chemical passivity of iron [48, 49], and chromium [48] with respect to acids: iron dissolves in concentrated sulfuric acid, while chromium dissolves in hydrochloric acid. The number of such examples could be extended considerably (see, for examples, [50-53]).

Ultra-Sonic Methods for the Physico-Chemical Study of Materials Which Are Important in Analytical Chemistry

Determination of the degree of hydration of ions in solution is of great importance in analytical chemistry. At present, among other methods, ultra-sonic methods are also used. [54-61]. Evaluation of the degree of hydration by means of ultra-sound may be carried out by two different methods [61], the most important of which is that suggested for the first time by Pasynskii [54]. The principle of this method may be briefly stated as follows. The electric field of an ion leads, in the surrounding layers of water, to some additional pressure which decreases the compressibility of the water. Since, at a small distance from the ion this pressure may have a considerable value, it is considered that the hydrated envelope of the ion is not subjected to compression. This signifies that the velocity of sound in this envelope is infinitely large. On the basis of results on the compressibility of solutions obtained from acoustic measurements, and under conditions where the compressibility of the hydrated envelope is assumed to be zero, it is possible to calculate the value of the hydration of the ions. Adiabatic compressibility is calculated by means of Laplace's equation:

$$c = \sqrt{\frac{1}{\beta_{\phi} \cdot \rho}},$$

where c is the velocity of sound, β_{ϕ} is the adiabatic compressibility; σ is the density. Calculation of the hydration h, expressed in grams of water per gram of dissolved material, for a solution 100 g of which contains g gram of dissolved material, is carried out on the basis of the formula:

$$h = \frac{\left(1 - \frac{\beta}{\beta_0}\right)(100 - g)}{g},$$

where β and β_0 are the compressibility coefficients of the solution and solvent (water) respectively.

Of some interest is the use of the value of adiabatic compressibility as a "property" in physico-chemical analysis. During a study of the compressibility – composition curve, sharp minima have been detected, the origin of which is ascribed to the formation of chemical compounds. Such an assumption has been confirmed experimentally by studying a number of systems; for example, the system ethyl acetate – analine. It has been known for some time that compounds possessing the molar composition 3 : 1, 3 : 2, and 1 : 1 exist in this system. It was found that the compressibility of these systems exhibit sharp minima at the molar compositions corresponding to the compounds indicated (Fig. 6) [62]. It has also been demonstrated that the value of the velocity of ultra-sound can be used directly, as a property for studying ternary mixtures [63]. It has been demonstrated, however, that the development of compounds in binary mixtures is not necessarily related to anomalous changes in the velocity of sound, and, on the other hand, the existence of the velocity of sound – composition curve of minima or maxima cannot always be related to the formation of a chemical compound [64].

It should also be pointed out that it is possible to identify organic compounds on the basis of the value of the molecular velocity of sound which exhibits additivity similar to that shown by molecular refraction, the parachor, or the Van-der-Waal's constant. The value of the molecular velocity of sound is calculated according to Rao's law:

$$R = c^{\frac{1}{3}} \frac{M}{\rho},$$

where M is the molecular weight; ρ is the density; c is the velocity of sound; and R is the molecular velocity of sound which is independent of temperature. It is also possible to determine the molecular weight of dissolved materials on the basis of the value of the molecular velocity of sound [2].

SUMMARY

Ultra-sound has already been used for solving many theoretical and practical problems in analytical chemistry. The further application of ultra-sound to chemical analysis may lead to a number of interesting results of practical importance.

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A STUDY OF THE FORMATION OF THE MIXED FERROCYANIDES OF COPPER AND THE ALKALI METALS BY A POTENTIOMETRIC METHOD

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The ferrocyanides of many metals are sparingly soluble, as the result of which they are being successfully used in a number of cases in analytical chemistry. The use of potassium ferrocyanide as a titrant during the visual and potentiometric determination of zinc, lead, indium, and other metals is widely known [1]. The potentiometric method, however, would seem to have more possibilities for the determination of various metals when the soluble ferrocyanides of the alkali metals are used as titrants, since there is then no need to select indicators for fixing the equivalence point. Potentiometric titration with potassium ferrocyanide is used nowadays with varying degrees of success for the determination of zinc, cadmium, cerium, lanthanum, gallium, indium, nickel, cobalt, and other metals. Despite all the advantages of the potentiometric method, it does possess the drawback that the position of the equivalence point often depends on the nature of the alkali metal entering into the composition of soluble ferrocyanide used as titrant, and also depends on the concentration of the ferrocyanide in solution. A knowledge of the details of the mechanism of formation of the insoluble mixed ferrocyanide opens up new possibilities for the analytical use of the ferrocyanides. In particular, it is essential to make a more careful study of the relationship between the composition of the mixed ferrocyanides and the presence in solution of one or other of the alkali metals, and the concentration of the latter. Treadwell and Hall [2] have already noted the shift in the equivalence point during the potentiometric titration of certain divalent metals salts by means of $K_4[Fe(CN)_6]$ in the absence and in the presence of cesium in solution. Subsequently, similar phenomena have been observed by other authors in other cases. Considerably more information regarding this point has been obtained by the solubility method. Nevertheless, as experiment shows, far from all the mixed ferrocyanides whose formation is fixed by the results of solubility, find reflection on the potentiometric titration curves taken in the same systems.

The present article is devoted to the potentiometric titration of copper ions by $[Fe(CN)_6]^{4-}$ ions. Despite a number of published articles on this question, no reliable potentiometric method of determining copper by means of a ferrocyanide has been put forward. Of the papers dealing with this problem, mention should be made of attempts to improve the results by titrating in an ammoniacal medium [3, 4]. Nevertheless, in all these papers, $K_4Fe(CN)_6$ was used as the titrant; the possible effect of other alkali metals present in solution – in addition to potassium – on the titration has not been studied. Convincing proof has been brought forward in some articles to suggest that there is a decrease in solubility of the mixed copper ferrocyanides with decreasing ionic radius of the alkali metal which enters into the composition of the respective precipitates [5-7]. All the same, no studies have been made of a system consisting of Cu^{2+} ions and $Me_4[Fe(CN)_6]$, where Me = Li, Na, K, Rb, Cs. The present article is an attempt to fill this gap.

Determination of the oxidation – reduction potential was carried out on an LP-6 potentiometer, using a platinum indicator electrode and a saturated calomel electrode.

First of all, experiments were carried out in which cupric sulfate solutions containing small amounts of ferricyanide, were titrated with potassium ferrocyanide. For this titration the following amounts were taken: 10 ml of 0.05 M cupric sulfate to which was added 10 ml of 1 N H_2SO_4; water was added to bring the total volume to 50 ml; 0.025 M potassium ferricyanide was added in amounts ranging from one drop to 0.5 ml. Under these conditions formation of a sparingly soluble copper ferricyanide was observed. Titration was carried out with 0.025 M potassium ferrocyanide with careful stirring. The oxidation–reduction potential of the solution changed very little up to the point where potassium ferrocyanide had been added to the cupric sulfate solution in an amount which was approximately 120% of that required for the formation of a normal copper ferrocyanide $Cu_2[Fe(CN)_6]$. Subsequently, there was observed a scarcely perceptible increase in potential, presumably, as the result of the formation of copper ferrocyanide from the ferricyanide which was obtained on addition of potassium ferricyanide to the cupric sulfate. As a result of this there occurred some increase in the concentration of $[Fe(CN)_6]^{3-}$ ions, and consequently an increase in the oxidation–reduction potential, after which, depending on the amount of potassium ferrocyanide added, there started a comparatively smooth drop in the oxidation–reduction potential.

Thus, these experiments showed that, during titration with potassium ferrocyanide of a cupric sulfate solution to which potassium ferricyanide had been added, there are no sharp changes in the value of the oxidation–reduction potential. Neither was there observed a characteristic jump on the curve for the oxidation–reduction potentials, so that it is impossible to establish exactly the composition of the mixed ferrocyanide of copper and potassium formed. Accordingly, during further work, titration was carried out with a solution of potassium ferrocyanide to which had been added a small amount of potassium ferricyanide. It was assumed, in this case, that there would be observed an increase in the oxidation–reduction potential towards the end of titration, when, presumably, formation of ferrocyanide at the expense of ferricyanide would occur. It was deemed most rational to carry out the titration using a potassium ferrocyanide solution to which 1% of ferricyanide had been added (1% with respect to the ferrocyanid In such cases a fairly large increase in the oxidation–reduction potential was observed. The cupric sulfate was titrated in acid media. To 10 ml of 0.05 M curpic sulfate was added 10 ml of 2 N H_2SO_4 for preventing formation of basic copper salts. As tests had shown, during titration in a strongly acid medium a more clearly defined potential change can be observed. It is possible that this is determined by an increase in the solubility of copper ferricyanide. It should be noted that during titration in an acid medium, the curve for the oxidation–reduction potentials is located in a higher position than when ordinary solutions are used.

The maximum on the oxidation–reduction potential curve, which corresponds to the highest concentration of ferricyanide ions with respect to $[Fe(CN)_6]^{4-}$ ions is observed, in this case, on addition of about 120% of potassium ferrocyanide with respect to the amount of this compound which is necessary for the formation of the normal copper ferrocyanide. The maximum corresponds to that point at which the copper ions are combined mainly in the form of ferrocyanide and the minimum excess of titrant has been added to the solution. As a result of such an addition, and as a result of the expulsion of $[Fe(CN)_6]^{3-}$ from the precipitate by $[Fe(CN)_6]^{4-}$, there is formed in solution a temporary enhanced concentration of the first type of ions with respect to the latter. On titrating further, the concentration of $[Fe(CN)_6]^{4-}$ increases rapidly, as a result of which the oxidation–reduction potential starts to drop. The maximum on the oxidation–reduction potential curve corresponds to the formation of the mixed ferrocyanide of copper and potassium $K_4Cu_{10}[Fe(CN)_6]$ (or, $5Cu_2[Fe(CN)_6]$, $K_4[Fe(CN)_6]$). The concentration of potassium ions in solution was found to exert some influence on the composition of the mixed copper and potassium ferrocyanide. Thus, on addition of potassium chloride to one of the solutions during titration, there was observed a small shift in the maximum on the oxidation–reduction potential curve towards the formation of a compound containing a larger amount of potassium. In this case 122-125% of the potassium ferrocyanide required for the formation of the normal ferrocyanide was used up for the formation of the mixed ferrocyanide of copper and potassium.

Three series of experiments were carried out in order to clarify the composition of the mixed ferrocyanides of copper with the alkali metals.

In the first series of experiments oxidation–reduction potentials were determined during titration of cupric sulfate with potassium ferrocyanide containing 1% of potassium ferricyanide, rubidium or cesium chloride being added to the solution in amounts equivalent to that of the potassium (Table 1, Fig. 1).

In the second series of experiments the cupric sulfate solution was titrated with sodium ferrocyanide containing 1% sodium ferricyanide, and also containing potassium, rubidium, or cesium chloride in amounts equivalent to that of sodium (Table 2, Fig. 2).

In the third series of experiments, titration was carried out with lithium ferrocyanide containing 1% of lithium ferricyanide, was well as sodium, potassium, rubidium, or cesium chloride in amounts equivalent to that of lithium (Table 3, Fig. 3).

The solutions of lithium and sodium ferrocyanides were prepared from potassium ferrocyanide via lead ferricyanide. Lead ferrocyanide was carefully washed free from potassium and then heated on a water bath with sodium carbonate solution, or with a suspension of lithium carbonate, taken in amounts which were 80% of the equivalent amount with respect to $Pb_2[Fe(CN)_6]$. The solutions obtained were filtered, and their concentrations established by titration with potassium permanganate in 1 N H_2SO_4. Sodium and lithium ferricyanides were prepared by oxidation of the corresponding ferrocyanides with chlorine water.

TABLE 1

Titration of 10 ml of 0.05 M $CuSO_4$ Solution with 0.025 M $K_4[Fe(CN)_6]$ (containing $K_3[Fe(CN)_6]$) in the Presence of Chlorides of Alkali Metals

a		b		c	
$K_4[Fe(CN)_6]$ In ml	In millivolts	$K_4[Fe(CN)_6]$+ + RbCl In ml	in millivolts	$K_4[Fe(CN)_6]$+ + CsCl In ml	in millivolts
0,0	725	0,0	730	0,0	730
1,0	750	1,0	750	1,0	750
10,0	755	10,0	750	10,0	750
11,0	765	12,5	765	15,0	755
11,5	790	14,0	795	18,5	770
11,9	820	14,5	850	18,7	785
12,0	825	14,8	870	18,8	850
12,1	825	14,9	870	19,0	915
12,2	795	15,0	875	19,2	940
12,3	790	15,1	860	19,3	950
12,4	770	15,2	850	19,4	900
12,6	660	15,4	680	19,6	755
13,0	600	15,7	640	20,0	725
13,5	585	17,0	615	21,0	685

The results of these experiments are given in Tables 1, 2, and 3 and in Figs. 1, 2, and 3. The amount of the alkali metal ferrocyanide (expressed as a percentage of the amount required for formation of the normal ferrocyanide of copper) is plotted along the abscissa, while the oxidation-reduction potential, in millivolts, is plotted along the ordinate.

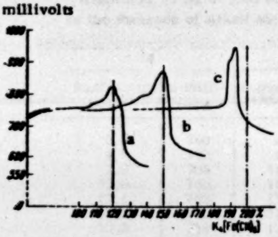


Fig. 1. Change in oxidation-reduction potential during titration of $CuSO_4$ by means of the solutions: a) $K_4[Fe(CN)_6]$; b) $K_4[Fe(CN)_6]$ + + RbCl; c) $K_4[Fe(CN)_6$ + CsCl.

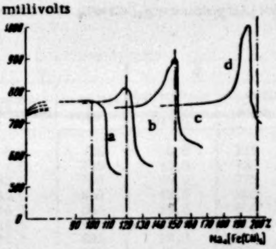


Fig. 2. Change in oxidation-reduction potential during titration of $CuSO_4$ by means of the solutions: a) $Na_4[Fe(CN)_6]$; b) $Na_4[Fe(CN)_6]$ + KCl; c) $Na_4[Fe(CN)_6]$ + + RbCl; d) $Na_4[Fe(CN)_6]$ + CsCl.

In Fig. 1 (curve a) is shown the change in oxidation-reduction potential during titration of cupric sulfate with potassium ferrocyanide. Initially, the curve goes almost parallel to the abscissa; afterwards, towards the end of titration, there is observed some increase in the potential. The potential reaches a maximum and then, comparatively slowly, decreases. During titration with potassium ferrocyanide the maximum is observed after addition of 120-123% of ferrocyanide. On addition to this same solution of potassium ferrocyanide, of rubidium chloride (curve b) and cesium chloride (curve c), in amounts equivalent to the potassium, the highest potential is observed at 150% and

192-193% respectively for ferrocyanide. Addition of sodium and lithium chlorides to potassium ferrocyanide, as was to be expected, has no effect on the position of the maximum on the curve as compared with curve a.

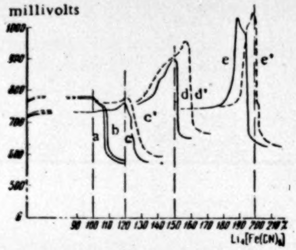


Fig. 3. Change in oxidation–reduction potential during titration of $CuSO_4$ by means of the solutions: a) $Li_4[Fe(CN)_6]$; b) $Li_4[Fe(CN)_6]$ + + NaCl; c and c') $Li_4[Fe(CN)_6]$ + + KCl; d and d') $Li_4[Fe(CN)_6]$ + RbCl; e and e') $Li_4[Fe(CN)_6]$ + CsCl.

In Fig. 2 are shown the curves illustrating changes in the oxidation–reduction potential during titration with sodium ferrocyanide. When only sodium ions were present, the highest potential was observed on addition of 99.8-100% of ferrocyanide (Curve a). On addition of potassium chloride to the sodium ferrocyanide (Curve b), the maximum potential was established on addition of 120-122% of ferrocyanide, i.e., on addition of the same amount of sodium ferrocyanide as during titration with potassium ferrocyanide. During titration with sodium ferrocyanide to which had been added an equivalent amount of rubidium chloride, the maximum potential (Curve c) was observed on addition of 149.4-149.8% of ferrocyanide, i.e., on addition of the same amount of ferrocyanide as that used during titration with potassium ferrocyanide in the presence of rubidium chloride. On addition of rubidium chloride, the potential reached a higher value, while the increase and decrease in potential occurred more sharply than in the case where potassium chloride was added.

Diagram 3 (Fig. 3) was constructed on the basis of the results obtained during titration with lithium ferrocyanide. In this case again, the same regularity was observed in the values of the oxidation–reduction potential as that observed during titration with sodium ferrocyanide. Thus, in the presence of only lithium, or of lithium and sodium, the highest value of the potential was observed on addition of 99.2% of ferrocyanide with respect to the amount necessary for formation of $Cu_2[Fe(CN)_6]$ (Curves a and b). Under these conditions the maximum is poorly defined; the drop in potential proceeds extremely slowly in the presence of excess ferrocyanide.

TABLE 2

Titration of 10 ml of 0.05 M $CuSO_4$ Solution (with 0.025 M $Na_4[Fe(CN)_6]$ containing $Na_3[Fe(CN)_6]$ in the Presence of Alkali Metal Chlorides).

a		b		c		d	
$Na_4[Fe(CN)_6]$ in ml	in millivolts	$Na_4[Fe(CN)_6]$+ +KCl in ml	in millivolts	$Na_4[Fe(CN)_6]$+ +RbCl in ml	in millivolts	$Na_4[Fe(CN)_6]$+ +CsCl in ml	in millivolts
0,0	740	0,0	730	0,0	725	0,0	725
1,0	760	1,0	750	1,0	745	15,0	750
9,9	765	11,0	755	13,0	750	18,0	775
10,0	765	11,5	775	14,0	800	18,5	800
10,1	762	11,8	800	14,5	850	18,8	850
10,2	760	11,9	805	14,8	875	18,9	925
10,3	755	12,0	810	14,9	895	19,0	950
10,5	745	12,1	805	15,0	900	19,1	975
10,6	740	12,2	795	15,1	885	19,2	985
10,7	735	12,3	780	15,2	675	19,3	990
10,8	580	12,4	750	15,3	655	19,4	995
10,9	565	12,5	650	15,4	650	19,5	1000
11,0	560	12,7	625	15.5	645	19,6	750
10,5	540	13,0	575	16,0	635	19,8	720
12,0	525	14,0	560	16,5	625	20,0	700

On addition of potassium chloride (Curve c) the maximum was observed at 120-122%. After the maximum, the potential decreased slowly. On addition of rubidium chloride (Curve d) the maximum was found on the addition of 149.8% ferrocyanide. In this case there was a comparatively large increase in potential while its drop was expressed clearly.

On addition of cesium chloride (Curve e) the maximum was observed at 189-190% with a sharp increase and decrease in the value of the potential. On addition of a large excess of cesium chloride, a shift in the maximum was observed. Thus, on addition of cesium chloride in an amount 2.5 times the equivalent amount of the element with respect to lithium, the maximum value of the oxidation–reduction potential was observed on addition of 198% ferrocyanide (Curve e'). In this latter case cesium chloride was added to the cupric sulfate.

TABLE 3

Titration of 10 ml of 0.05 M $CuSO_4$ with a Solution of $Li_4[Fe(CN)_6]$ (containing $Li_3[Fe(CN)_6]$) in presence of alkali metal chlorides)

a		b		c		d		e		c'		d'		e'	
In ml	In milli-volts	In ml	In milli-volts	In ml	In milli-volts	In ml	In milli-volts	In ml	In milli-volts	In ml	In milli-volts	In ml	In milli-volts	In ml	In milli-volts
0,0	750	0,0	745	0,0	730	0,0	725	0,0	740	0,0	740	0,0	725	0,0	730
1,0	780	1,0	775	10,0	750	1,0	735	18,0	760	11,5	785	1,0	735	18,0	750
9,9	780	9,0	775	11,5	755	12,5	755	18,5	825	11,7	785	12,5	760	19,1	800
10,0	765	10,0	765	11,7	760	13,5	770	18,6	850	11,9	790	13,5	805	19,2	850
10,1	765	10,1	765	11,8	765	14,0	825	18,7	875	12,0	795	14,5	850	19,3	900
10,2	762	10,2	760	11,9	765	14,5	850	18,8	950	12,1	800	14,5	885	19,4	950
10,3	760	10,3	760	12,0	770	14,7	880	18,9	1025	12,2	800	15,8	905	19,5	1000
10,4	760	10,4	755	12,1	760	14,9	900	19,0	1085	12,3	795	15,5	940	19,7	1010
10,5	755	10,5	750	12,2	725	15,0	900	19,1	955	12,4	785	15,6	955	19,8	1045
10,6	750	10,6	750	12,3	720	15,1	890	19,2	990	12,5	780	15,7	950	19,9	1035
10,7	700	10,7	700	12,4	665	15,2	675	19,3	985	12,6	750	15,8	945	20,0	1025
10,8	615	10,8	620	12,5	650	15,3	660	19,4	980	12,8	700	15,9	925	20,1	1760
10,9	610	10,9	615	12,6	610	15,5	655	19,5	675	13,0	675	16,0	750	20,3	675
11,0	600	11,0	610	13,0	600	16,0	650	19,6	660	13,5	635	16,2	290	20,4	660
11,5	575	11,5	580	14,0	575	17,0	645	20,0	635	14,0	615	17,0	675	21,0	625

The shift in the maximum on the oxidation–reduction potential curve was also observed on addition of excess rubidium chloride. Thus, on addition of rubidium in an amount which was 2.5 times the equivalent amount of this element with respect to lithium, the maximum was observed on addition of 156-158% of ferrocyanide (Curve d').

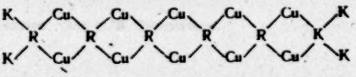
It is necessary to point out that on addition of rubidium chloride to the ferrocyanides of lithium, sodium, and potassium in an equivalent amount, the maximum value of the oxidation–reduction potential was always obtained on addition of ferrocyanide in an amount very near to 150% of the amount required for the formation of $Cu_2[Fe(CN)_6]$.

During formation of the mixed ferrocyanide of copper and potassium, excess of added potassium chloride also led to a displacement of the maximum of the oxidation–reduction potential. Thus, on addition of potassium ions in an amount 2.5 times greater than that equivalent to lithium, the maximum was obtained on addition of about 125% of the ferrocyanide required for formation of $Cu_2[Fe(CN)_6]$. In this case a slower drop in the oxidation–reduction potential was observed during the first period after the maximum (Curve c').

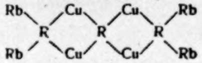
It should be pointed out that the position of the maximum on the oxidation–reduction potential curve during formation of the mixed ferrocyanide of copper and potassium is less stable than in the case of the copper and rubidium ferrocyanide.

It can be concluded from Figs. 1, 2, and 3 that during precipitation of copper salts with lithium or sodium ferrocyanide, the normal copper ferrocyanide is formed $Cu_2[Fe(CN)_6]$.

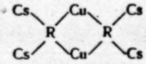
In the presence of potassium ions, since the maximum of the oxidation–reduction potential corresponds to the addition of about 120% of ferrocyanide, the mixed ferrocyanide of copper and potassium is formed $K_4Cu_{10}[Fe(CN)_6]_6$ or written otherwise $5Cu_2[Fe(CN)_6] \cdot K_4[Fe(CN)_6]$. The structure of this salt may be represented as follows:



In the presence of rubidium ions, in the case where this element is added in amounts equivalent to lithium, sodium, or potassium, the maximum is observed on addition of 150% of ferrocyanide; this corresponds to the formation of a mixed ferrocyanide of copper and rubidium $Rb_4Cu_4[Fe(CN)_6]_3$ or $2Cu_2[Fe(CN)_6] \cdot Rb_4[Fe(CN)_6]$:



On addition of a large excess of cesium salts, the maximum oxidation–reduction potential is observed on addition of 200% of ferrocyanide with respect to that necessary for formation of $Cu_2[Fe(CN)_6]$. In this case, obviously, the mixed ferrocyanide $Cs_2Cu[Fe(CN)_6]$:



is formed.

SUMMARY

It has been established that the equivalence point, corresponding to a break or to a maximum on the potentiometric titration curves, depends on the nature of the alkali metal present in solution. During titration with lithium or sodium ferrocyanide, $Cu_2[Fe(CN)_6]$ is formed. In the presence of the ions of the remaining alkali metals mixed ferrocyanides are formed:

$$K_4Cu_{10}[Fe(CN)_6]_6,\quad Rb_4Cu_4[Fe(CN)_6]_3 \text{ and } Cs_2Cu[Fe(CN)_6].$$

The potentiometric method which shows that greatest possibilities for the determination of copper is titration with rubidium ferrocyanide or titration with the ferrocyanides of the other alkali metals in the presence of rubidium salts.

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* Original Russian pagination. See C. B. Translation.

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MICROCRYSTALLINE REACTIONS IN MELTS

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An article was published not very long ago [1] in which it was suggested that microcrystalloscopic reactions for certain ions could be carried out by using molten 8-hydroxyquinoline, both as a reagent and as a medium for carrying out the reactions; in the molten drop it is possible to observe crystalline reaction products with copper, zinc, calcium and other salts. Molten 8-hydroxyquinoline has also been used in color reactions for iron and vanadium [2]. Other authors [3] have carried out a color reaction for bismuth with dithizone, using a solution of this reagent in naphthalene for this purpose.

We have tested some reagents dissolved in low melting organic compounds for microcrystalloscopical analytical purposes and have observed some very interesting results. Some reagents, 8-hydroxyquinoline among them, used as media for carrying out microreactions, did not prove suitable. With such reagents it was only possible to work at temperatures higher than their melting points. On cooling below this temperature, the material crystallized rapidly, and the crystals of the solvent itself (the medium) prevented observation of the crystalline reaction products.

TABLE

Dimensions of Nickel Dimethylglyoximate Crystals

Nickel content of test sample, in γ	Solvent	
	Benzophenone	Aqueous ammonia solution
	Maximum dimensions of the crystals, in μ	
1	1000	30
0.5	600	30
0.1	400	25
0.05	150	20
0.025	50	15

We used reagents dissolved in molten benzophenone (m.p. 48°) or salol (m.p. 42°). The use of salol, and, particularly benzophenone, proved to be very convenient because of their capacity to supercool. A molten drop, containing reagent and reaction product, retained its liquid state on cooling to room temperature, and remained in that state for a long time. We succeeded in keeping preparations in benzophenone in a liquid state over periods of 5-6 days; in individual cases considerably longer; in the case of salol the preparations remained liquid for only 24 hours.

Detection of nickel with dimethylglyoxime was carried out as follows. 2 mg of dimethylglyoxime was dissolved in 1 g of molten benzophenone or salol and the solution transferred to a mortar. After cooling, a small crystal of benzophenone (or salol) was added for seeding; the mass thereupon solidified rapidly; it was then ground to a powder. A drop of a solution of a nickel salt was heated on a microscope slide to evaporate the water. To this dry residue was added a few grains of the solution of diemthylglyoxime in benzophenone (or salol) and the whole heated to the molten state. After a few minutes the slide was examined under the microscope. When these conditions were used, red, very large, and well-formed crystals of nickel dimethylglyoximate could be observed. (Fig. 1).* The crystal size gradually increased. When nickel was detected in aqueous or aqueous-ammoniacal media, the crystals obtained were almost invariably considerably smaller (see Table).

The crystals formed in salol were smaller than those obtained in benzophenone.

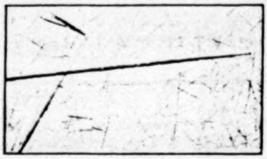

Fig. 1. Nickel dimethylglyoximate crystals (solvent – benzophenone).

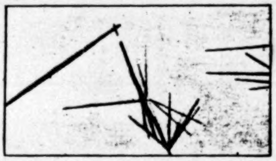

Fig. 2. Nickel α-benzyldioximate crystals (solvent – benzophenone).

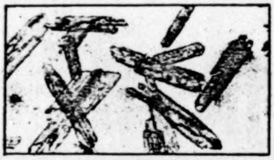

Fig. 3. Crystals of $C_9H_7N \cdot H[BiI_4]$ (solvent – diphenylamine).

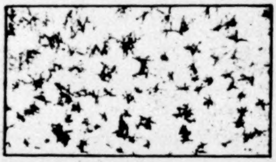

Fig. 4. Crystals of $C_9H_7N \cdot H[BiI_4]$ (solvent – water).

Using α-benzyldioxime in a benzophenone medium we were able to obtain with nickel salts, large, bright-red, needles with particle sizes amounting to 300 μ in length (Fig. 2). Next we investigated a number of microcrystalloscopic reactions for bismuth, based on the formation of the compound $BH[BiI_4]$ (where B is a base), characterize by an intense color, and often recommended for detection of bismuth [4]. The reagent was a solution of a suitable base and ammonium iodide in a readily fusible organic compound. When this reaction was carried out using ammonium iodide, the results obtained were unsatisfactory. Only by using quinoline diethylate ($C_9H_7NC_2H_5$) dissolved in molten diphenylamine (m.p. 53.5°) was it possible to detect bismuth clearly. 2 mg of the reagent indicated was dissolved in 1 g of molten diphenylamine; after cooling and solidifying the solid solution was ground to a powder. The reagent was placed on, and fused on, the still moist residue obtained on a microscope slide by evaporation of a drop of a bismuth salt. Dark-red crystals 200-300 μ long were obtained (Fig. 3). These crystals could readily be observed even in those cases where the diphenylamine itself crystallized during cooling. The crystals obtained in aqueous media were no longer than 50-60 μ (Fig. 4). Replacement of diphenylamine by benzophenone or salol led to the formation of small crystals. Lead salts reacted with quinolinediethylate dissolved in diphenylamine to give reaction products in the form of almost colorless needles up to 150 μ long.

SUMMARY

The use of certain organic reagents dissolved in molten, indifferent organic compounds, leads, in a number of cases, to the formation of large crystals. Microcrystalloscopic reactions for nickel are described in which nickel reacts with dimethylglyoxime and α-benzyldioxime respectively, in a medium of molten benzophenone; reactions are also described for detecting bismuth and lead, using quinolinediethylate in a medium of molten diphenylamine.

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* All the micro-photographs were obtained using a magnification of 150.

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THE APPLICATION OF DIPHENYLCARBAZONE FOR THE PHOTOMETRIC DETERMINATION OF COPPER IN IRON AND STEEL

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A number of photometric techniques have been proposed in recent years for the determination of copper in iron and steel [1-9]. However, many of them require reagents which are not readily available, or special apparatus, and this limits the possibilities of their practical application. Our observations have shown that, compared with the techniques described, a much more convenient method for the microdetermination of copper, is a very sensitive test based on the interaction of copper with diphenylcarbazone to form a complex which is sparingly soluble in water. Hydrogen ion concentration has a considerable effect on the formation of the complex; the optimum conditions for carrying out the reaction lie within the pH limits 4-5.

The copper derivative of diphenylcarbazone is insoluble in water, and only sparingly soluble in amyl alcohol, ether, and carbon tetrachloride; it dissolves readily in benzene and its homologs. The red solutions of the complex conform to the Lambert-Beer law.

Under the conditions indicated, diphenylcarbazone does not form benzene-soluble compounds with WO_4^{2-} the following ions: Ag^{+}, $AuCl_4^{-}$, Zn^{2+}, Al^{3+}, Sn^{2+}, $V_2O_7^{4-}$, Sb^{3+}, Bi^{3+}, WO_4^{2-}, F^{-}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, UO_2^{2+} Ni^{2+}, Cr^{3+}, $PtCl_6^{2-}$, $B_4O_7^{2-}$, Ti^{4+}, Tl^{+}.

With mercury, diphenylcarbazone only reacts in the same way as copper when chlorides are absent; while diphenylcarbazone reacts with molybdenum, cadmium, and lead at high concentrations of these metals which exceed the copper content several thousand times.

The reaction is very sensitive and permits detection of tenths of a microgram of copper.

In developing a quantitative method of determining copper in steel and iron by means of the reaction described, it was necessary, in the first instance, to resolve the problem of getting a completely transparent solution during the extraction of the copper-diphenylcarbazone complex with benzene, since the presence of even the slightest turbidity leads to a considerable experimental error as the result of the partial adsorption of the copper complex by this turbidity.

Another undesirable feature proved to be precipitation of iron as hydroxide which possesses a similar adsorptive capacity with respect to copper ions [10-12].

Necessary Reagents. An alkaline solution of phenolphthalein; this was prepared by weighing out 10 mg of phenolphthalein on a torsion balance and transferring it to a flask, to which was then added 1 ml of concentrated ammonia solution and 9 ml of twice distilled water. This solution was prepared daily. 2) A benzene solution of diphenylcarbazone * was prepared as follows; 10 mg of diphenylcarbazone was weighed out on a torsion balance and carefully placed in a 100 ml standard flask; 20-25 ml of benzene was added and the flask then placed in a beaker of hot water until complete solution of the crystals had been attained. The flask was then cooled and benzene added to bring the volume up to the mark; 0.4 ml of pyridine was finally added to accelerate the rapid

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* The commercial grade of diphenylcarbazone marked as analytical grade material could not be used without the preliminary treatment with potassium hydroxide and H_2O_2 described in L. M. Kul'berg's book, "Syntheses of Organic Reagents for Inorganic Analysis." Goskhimizdat, Moscow-Leningrad, 1947, p. 68.

formation of the copper complex.

Analytical Procedure. 100-250 mg of test material was weighed out on an analytical balance and transferred to a 100 ml Kjeldhal flask made of heat-resistant glass. 4 ml of twice-distilled water and 1 ml each of concentrated sulfuric and nitric acids were then added to the contents of the flask; then working with sparingly soluble samples of steel, 1 ml of concentrated hydrochloric acid was also added. The sample was dissolved by careful heating. On cooling, 0.5 ml of hydrogen peroxide was added and the contents of the flask heated until liberation of gas bubbles ceased.

1 ml each of concentrated sulfuric and nitric acids was added to the cooled contents of the flask, and the whole quantitatively transferred to a 250 ml standard flask; the volume was finally made up to the mark with water.

The copper content of the test material was established by measuring out 2 ml of the solution from the 250 ml flask into another Kjeldhal flask using a pipet with two marks on it; 0.2 g of a univalent metal phosphate was added to this aliquot and the whole shaken. After the salts had dissolved 0.5 ml of the alkaline phenolphthalein solution was added. To this same flask was added concentrated ammonia in an amount equal to twice the volume required to neutralize the acid in the test liquid. The slightly turbid solution was shaken until the turbidity had completely disappeared; the solution was then neutralized with a saturated solution of potassium dihydrogen phosphate which was added carefully from a buret. After this, the volume of water which it was necessary to add to bring the total volume of the liquid in the flask to 15 ml was calculated.

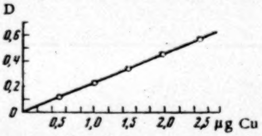

Fig. 1. Calibration curve. Filter S 53; layer thickness 10 mm.

When, during neutralization of the solution, a large volume of phosphate has to be used – this can happen as a result of the lowered solubility of the salt at a low temperature – in order to avoid increasing the volume to a value greater than 15 ml, it was found necessary to add about 0.5 g of crystalline phosphate first, and then add the requisite amount of reagent from a buret.

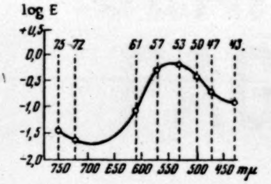

Fig. 2. Curve for the absorption of a solution of the copper-diphenylcarbazone complex in benzene.

To the completely clear solution treated in this way was added 5 ml of the benzene solution of diphenylcarbazone and the whole shaken thoroughly; after the layers had separated the benzene layer was transferred to a 5 or 10 mm photometer cell, depending on the intensity of the benzene layer. The adsorption was measured using a S 53 filter. The reference liquid placed in the other photometer cell was the solution of diphenylcarbazone in benzene used for extracting the copper.

The calibration curve was constructed by using a standard cupric sulfate solution containing 10 μg of copper per ml; during preparation of this solution, in order to prevent formation of basic salts, 10 ml of 10% sulfuric acid solution was added per 500 ml of liquid, after which the volume was made up to the mark with water. Having measured out aliquots of the standard solution into Kjeldhal flasks by means of a microburet, such that after making up to volume in 250 ml standard flasks, 2 ml of these final solutions contained 1, 2, 3, etc. μg of copper, the procedure outlined above for determination of copper in steel was followed. In order to promote more uniform boiling of the liquids in these cases, it was found necessary to add 2-3 glass beads to the contents of the Kjeldhal flasks. Furthermore, when determinations were made it was found essential to carry out a blank, since the reagents and water used in the work always contained copper.

Having measured the density of the solutions, a calibration curve was constructed (Fig. 1).

The absorption curve is shown in Fig. 2.

DISCUSSION OF RESULTS

In view of the exceptional sensitivity of the reaction, whereby it is possible, using a photometer, to detect hundredths of a microgram of copper, it is essential to treat the flasks, etc. used in the work, in order to avoid contamination with traces of copper, which will affect the results considerably. For this purpose it is recommended therefore that the flasks be washed with hot sulfuric acid, followed by hot concentrated ammonia; they are washed then several times with tap water, and finally, rinsed with twice-distilled water. Subsequently, in the course of the work, the flasks are washed several times with tap water, and twice with twice-distilled water.

TABLE 1

Results of Replicate Determinations of the Amount of Copper in the Same Sample of Test Material

Test material	Copper content, in %			Mean value
	I	II	III	
Stainless steel				
Sample I	0.207	0.205	0.209	0.207
Sample II	0.845	0.838	0.846	0.843
Instrumental steel				
Sample I	0.159	0.159	0.158	0.158_7
Sample II	0.132	0.134	0.134	0.133_3
Sample III	0.127	0.127	0.127	0.127
Sample IV	0.235	0.235	0.236	0.235_3
Iron				
Sample I (wire)	0.075	0.074	0.074	0.074_3
Sample II (sheet)	0.178	0.175	0.174	0.176
Sample III (wire)	0.092	0.095	0.092	0.093

All the solutions used in the course of the work should be prepared using twice-distilled water prepared in a glass distillation apparatus. The hands of the operator should not come in contact with any copper materials; balances with copper weighing pans should not be used either.

TABLE 2

Determination of Copper After Addition of Various Amounts of it to a Sample of Test Material

Test material	Copper content of the solution taken for analysis in μg	Amount of copper added to 2 ml of test solution, in μg	Calculated amount of copper, in μg	Amount of copper found, in μg	Error, in %
Stainless steel					
Sample I	4.015	0.5	4.515	4.7	+4.3
Sample II	15.848	1.0	16.848	16.780	−0.5
Sample III	5.193	3.0	8.193	8.171	−0.3
Sample IV	3.422	0.5	3.922	3.93	+0.2
Sample IV	3.216	1.0	4.216	4.191	−0.6
Iron					
Sample II (sheet)	2.05	1.2	3.25	3.33	+2.4
Sample II "	3.67	0.7	4.37	4.45	+1.8
Sample II "	1.66	2.0	3.66	3.50	−4.4
Sample II "	2.09	0.5	2.59	2.63	+1.5

In order to establish the reproducibility of the results obtained during determination of copper in the same test material, we carried out a series of tests of which the results are given in Table 1.

In order to establish the accuracy of the method, a series of experiments was carried out in which known amounts of copper were added to the test material (Table 2).

As the results given in Table 2 show, the experimental error does not exceed 4%.

A very important stage in this method is the complexing of iron as a soluble complex by addition of excess ammonia and sodium phosphate to the solution. This technique possesses several advantages over the technique of precipitating iron as the hydroxide, since it is possible by using the former, to obtain completely clear and colorless solutions which do not interfere with complete extraction of the copper complex.

In order to establish the amount of copper absorbed by precipitated ferric hydroxide when the normal technique is used, the following experiment was carried out. After a sample of steel had been dissolved and iron had been precipitated by means of ammonia, 100 ml of which was added, the amount of copper in the filtrate, whose volume had been made up to 250 ml, was found to be 0.1877%. The precipitate of ferric hydroxide, freed from solution by decanting and centrifuging, was quantitatively transferred to a Kjeldahl flask; after dissolution in a mixture of nitric and sulfuric acids, the solution was transferred to a 250 ml flask and precipitated again with 100 ml of concentrated ammonia. When this was done, another 0.0084% of copper was found. On precipitating for a third time only traces of copper were found. Thus, the total content of copper in the sample of steel taken was found to be 0.1961%. Determination of copper in the same sample of steel by the method we have suggested above gave a value of 0.207%.

By means of appropriate modification the method could be used for the "in situ" determination of copper in iron and steel.

SUMMARY

A method has been developed for the photometric determination of copper in iron and steel, using diphenylcarbazone. The copper derivative of diphenylcarbazone is insoluble in water but is readily extracted by benzene and its homologs; the intensity of the red benzene extract conforms to the Lambert-Beer law. The reaction describe is specific and highly sensitive. It permits detection of tenths of a microgram of copper. Iron is complexed as a phosphate complex. The experimental error for the determination of copper in iron and steel does not exceed 4%.

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THE POSSIBILITY OF USING MUREXIDE AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF ZINC

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Comparatively few good reagents are known for the photometric determination of zinc. Thus, dithizone, 8-hydroxyquinoline, and some other materials have found practical application for this purpose [1]. Dithizone and 8-hydroxyquinoline have been recommended as the best reagents, but they are not free from some drawbacks [2]. A possible reagent for the photometric determination of zinc is murexide (ammonium purpureate) which has recently found wide application in complexometry [3, 4]. Results have been given on the use of murexide for the photometric determination of calcium [5-9] while simple methods have been developed for synthesizing murexide [10], and for stabilizing its solutions [11] etc.

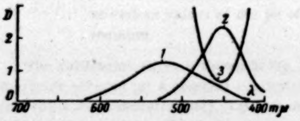

Fig. 1. Absorption curves for murexide (1), and its complex with zinc (2), and for light filter No. 7 with photometer FM (3).

Murexide interacts with the ions of many metals [5, 6, 12, 13] although in this connection the results are contradictory, for example with respect to the ions UO_2^{2+}, Th^{4+}, and Pb^{2+} [12-13]. The instability constants of many of the complexes formed have been determined [12]. A detailed study of the interaction of murexide with zinc ions, which one of us carried out in conjunction with Vestfried [14], has shown that purpuric acid forms a stable complex $Zn(H_3R)_2^{2-}$, whose instability constant is $K = 4.8 \cdot 10^{-10}$. It is essential that the absorption band for the complex (λ_{max} = 455 mμ) should be displaced appreciably with respect to the absorption band for murexide itself (λ_{max} = = 520 mμ), as is evident from Fig. 1. The reaction of murexide with zinc ions is very sensitive. The molar absorption coefficient of the complex ϵ_{max} amounts to 40,000.

It was of interest to establish the possibility of using murexide for the direct photometric determination of zinc. The murexide necessary for the work was synthesized from uric acid [15]. The finished product was carefully washed free from alloxantin by means of absolute ethanol. Aqueous murexide solutions were prepared in twice-distilled water. Purified zinc sulfate which had been analyzed gravimetrically was used as the source of zinc ions. A spectrodensograph [16] as well as an FM photometer (vertical model) were used for carrying out photometric measurements of the solutions; for greater convenience the FM photometer was fixed in a horizontal position so that it was possible to use cells from the FEK-M photocolorimeter.

During measurements of the optical density over the range 0.5-0.8 in the FM photometer using a No. 5 filter (maximum transmission at λ_{max} = 525 m μ) the relative error did not exceed 0.6-0.7%, while on using a No. 7 filter (λ_{max} = 455 m μ), the error increased to 1.2-1.5%.

Murexide solutions, particularly in acid and alkaline media, are unstable with time. According to our results, at a pH from 6 to 8 it is possible to use solutions over a period of several hours, so that we always used freshly prepared solutions. The stability of murexide solutions when the latter are buffered increases slightly. In the presence of zinc ions the optical density of the solutions remains almost constant for 30-45 minutes. This period is quite sufficient for carrying out photometric measurements.

The optical density of solutions containing zinc ions and murexide is strongly dependent on the pH of the medium. For a ratio of the concentration of zinc ions to murexide of 1 : 6, the maximum optical density was observed at a pH of 10.5 (Fig. 2). Measurements were carried out on spectrodensograph at 460 mμ. The concentrations of the zinc ions (c_{Zn}) and murexide (c_R) were $4.2 \cdot 10^{-5}$ and $2.5 \cdot 10^{-4}$ mole/liter. The necessary pH was established by addition of hydrochloric acid or sodium hydroxide to mixtures of the original solutions. A similar curve was also obtained on using buffer solutions. As is evident from Fig. 2, the reaction is most sensitive at pH 10-11; however, the stability of the solutions with time decrease considerably. In this connection, in further work we worked at pH 7.5, which was established by means of a veronal buffer [17].

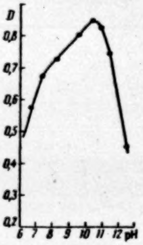

Fig. 2. Change in the optical density of solutions of the complex formed between zinc and murexide at various values of the pH of the medium.

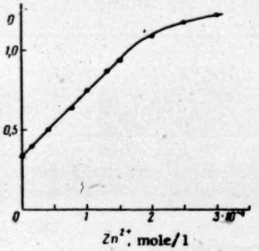

Fig. 3. Calibration curve. Photometer FM; light filter No. 7; thickness of layer in the cell 0.5 cm.

The calibration curve is shown in Fig. 3. The solutions were prepared by mixing equal volumes (10 ml each) of murexide solution (at a constant concentration of $c_R = 2.25 \cdot 10^{-3}$), buffer solution (with a pH of 7.5) and zinc sulfate (different concentrations). Optical density was measured within 5-7 minutes of mixing the solutions. The maximum concentration of zinc ions in the mixture amounted to $3 \cdot 10^{-4}$ mole/liter for a constant murexide concentration of $7.5 \cdot 10^{-4}$ mole/liter. As can be seen from Fig. 3., Beer's law is followed quite well up to a zinc concentration of $1.5 \cdot 10^{-4}$ mole/liter, i.e., up to a ratio of $c_R : c_{Zn} \geq 5$. Measurements were carried out with respect to a colorless glass plate fitted into the second beam of the apparatus; as a result of this the curve did not pass through the origin. Determination of zinc was found to be possible at concentrations as low as $2 \cdot 10^{-5}$ mole/liter. The reaction sensitivity can be increased by using longer cells and higher pH values.

TABLE 1

Reproducibility of the Determination of Zinc by Means of Murexide

Test No.	$c = 3{,}0 \cdot 10^{-5}$		$c = 7{,}5 \cdot 10^{-5}$		$c = 1{,}3 \cdot 10^{-4}$	
	D	$c \cdot 10^{5}$	D	$c \cdot 10^{5}$	D	$c \cdot 10^{4}$
1	0,47	3,1	0,64	7,4	0,85	1,27
2	0,45	2,9	0,65	7,5	0,88	1,32
3	0,47	3,1	0,64	7,4	0,86	1,28
4	0,47	3,1	0,66	7,8	0,87	1,30
5	0,45	2,9	0,64	7,4	0,87	1,31
6	0,46	3,0	0,65	7,5	0,86	1,28
7	0,47	3,1	0,66	4,8	0,87	1,30
$\bar{c}$	$(3{,}03 \pm 0{,}09) \cdot 10^{-5}$		$(7{,}5 \pm 0{,}17) \cdot 10^{-5}$		$(1{,}29 \pm 0{,}02) \cdot 10^{-4}$	
δ	3%		2,3%		1,5%	

In order to evaluate the reproducibility of the method, replicate determinations of zinc were carried out at three different concentrations. The solutions were prepared as indicated above. From the results given in Table 1 it is evident that the relative error (δ %) for the determination of mean values of c_{Zn} does not exceed ± 3%. Calculations were made at a confidence level of $\alpha = 95\%$. [18].

TABLE 2

Effects of Certain Metals on the Determination of Zinc (initial concentration of zinc – $c_{Zn} = 5 \cdot 10^{-5}$ M)

Test No.	Cu		Cr		Al			
	$c \cdot 10^5$	D	$c \cdot 10^5$	D	$c \cdot 10^5$	D	$c \cdot 10^5$	D
1	0,0	0,390	0,0	0,388	0.0	0,390	0,0	0,470
2	1,0	0,389	0.3	0,386	1.0	0,385	1.0	0,468
3	5,0	0,405	1,0	0,370	5,0	0.388	5,0	0,466
4	10,0	0,460	—	—	10.0	0,386	10.0	0,467
5	16,0	0,515	—	—	25.0	0,335	20.0	0,465
6	—	—	—	—	45,0	0,323	50,0	0,466
7	—	—	—	—	—	—	60,0	0,451
pH	7,3		7,3		7,3		10,3	

Thus, experiments with pure solutions of zinc sulfate showed that murexide actually behaves as a very sensitive reagent for zinc ions, and can be used for its photometric determination. All the same, because of the low selectivity of murexide, difficulties may arise when attempts are made to use it for the determination of zinc in actual test materials.

The possibility of using murexide for the photometric determination of zinc was considered from the point of view of analyzing aluminum alloys containing approximately 10% zinc, 3% copper, 0.5% chromium, and 86-87% aluminum. In order to check on interference from copper, chromium, and aluminum during determination of zinc with murexide, solutions were prepared with a constant zinc concentration ($5 \cdot 10^{-5}$ M) and variable amounts of the foreign metals (Table 2). For this purpose 10 ml of $9.0 \cdot 10^{-4}$ M murexide solution was mixed with 5 ml of buffer solution, 10 ml of $1.5 \cdot 10^{-4}$ M zinc sulfate, and 5 ml of the solution (with varying concentrations) of the corresponding metal sulfate. Table 2 contains the results obtained for the optical density of the solutions; it is clear from these results that at pH 7, aluminum in an amount twice that of zinc, cannot be tolerated (the solutions become turbid on account of the formation of the hydroxide), while the permissible limit for copper or chromium (taken separately) is not more than one fifth of the amount of zinc. By working at a pH > 10, aluminum in amounts which are ten times that of the zinc can be tolerated, since, under these conditions, the hydroxide dissolves. The results obtained show that by using an alkali method for dissolving the aluminum alloys, and then removing the non--amphoteric hydroxides, it is possible to determine zinc in the presence of a large amount of aluminum. In alloys of the type considered above, the ratio of Cr to Zn is approximately 1 : 20, which is considerably less than the permissible limit (1 : 5, as can be seen from Table 2); consequently, the presence of chromium in an alkali solution will not interfere with zinc determination.

SUMMARY

1. The possibility of using murexide for the photometric determination of zinc has been investigated.

2. Experiments have shown that at pH 7.5, solutions conform to Beer's law at zinc concentrations up to $1.5 \cdot 10^{-4}$ mole/liter, when the murexide concentration of the solution is $7.5 \cdot 10^{-4}$ mole/liter.

3. Determination of zinc is possible at a concentration of $2 \cdot 10^{-5}$ mole/liter. On increasing the pH to 10-11, the sensitivity of the reaction increases considerably.

4. The effect of copper, chromium, and aluminum (which accompany zinc in certain aluminum alloys) on the photometric determination of zinc by means of murexide has been studied.

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H-RESORCINOL AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF BORIC ACID

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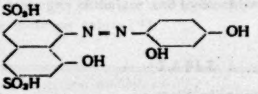
The hydroxyanthraquinones alizarin, quinalizarin, carminic acid and others containing the hydroxyl group in the para position with respect to the quinone group have been used for the photometric determination of boric acid. Brightly colored solutions of these hydroxyanthraquinones in concentrated sulfuric acid, on addition of boric acid, change their color.

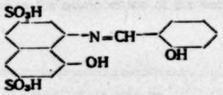
Other organic compounds containing a hydroxyl group adjacent to the carbonyl group, e.g., resacetophenone [1], and the dye chromotrope 2B [2] in the tautomeric hydrazo-form, also react with boric acid in sulfuric acid medium.

In other methods the reaction of boric acid with the dibenzoyl methane derivative curcumin has been used. Dyes which are salicylic acid derivatives behave in a similar way to curcumin on evaporating their acid solutions; the reaction sensitivity is, however, low [3].

In contrast to these color reactions which are carried out in concentrated sulfuric acid, or by removing water by evaporation, reactions have been found which can be carried out in weak acetic acid solutions [4]. Compounds containing two hydroxyl groups in adjacent para- and ortho-positions to the azo- or azomethine group can act as reagents:



H-resorcinol (8-hydroxy-3,6-disulfonaphthalene < 1-azo-1'> > −2', 4'-dihydroxybenzene)



The azomethine derived from H-acid and salicaldehyde

On carrying out the reaction with the azo dye derived from diazotized H-acid and resorcinol, the color of the solution changes from yellow to rose, while the second compound − azomethine − gives a bright-yellow color in acetic acid solutions of boric acid. It has been shown [4-5] that both of these reagents can be used for the photometric determination of boron.

We set out to study the composition and properties of the compound formed between boron and the dye H-resorcinol, and to determine the dissociation constant, the molar extinction coefficient, the effect of the pH of the solution, and the time for complete formation of the compound.

Composition of the Compound formed between H-resorcinol and Boric Acid. In order to determine the stoichiometric ratio between boric acid and H-resorcinol in the compound formed by them, using the method of "continuous variation" [6], stock 10^{-3} M solutions of boric acid and H-resorcinol were prepared (H-resorcinol − 0.044%, boric acid − 0.0062%). The solutions were acidified with 1 N acetic acid:

Into a series of 50 ml standard flasks were pipetted various amounts of boric acid and reagent, the amounts taken being such that the total final volume in each case was 5 ml. The procedure followed was to pipet the boric acid solution into a flask first; this was then diluted to 25-30 ml, 5 ml of acetic acid was then added by means of a pipet; the H-resorcinol was next added and the volume made almost up to the mark with water. The solutions were heated on a water bath to approximately 95° for 5-10 minutes; the flasks were then cooled and the volume made up the mark, the flasks were finally allowed to stand for 24 hours. The light absorption of the solutions was measured on a type FM universal photometer using a M-53 filter (maximum transmission at 530 mμ).

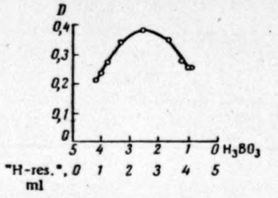


Fig. 1. Determination of the composition of the compound formed between boric acid and H-resorcinol.

The light absorption was measured as follows: into one 50 mm cell was introduced the test solution of boric acid plus reagent, while into the other was introduced a solution containing the same amount of boric acid.

The results obtained were the means of three readings.

As is evident from Table 1 and Fig. 1, the maximum light absorption is observed at a ratio of 1 : 1 of the volumes of boric acid to reagent. This means that in the compound formed there is one molecule of boric acid per molecule of H-acid. This confirms the formula suggested previously for this compound of boric acid with H-resorcinol.

Dissociation Constant of the Compound Formed Between Boric Acid and H-Resorcinol in Solution

In order to determine the dissociation of the boric acid – H-resorcinol complex, measurements were carried out at three pH's, namely 2.2, 2.6, 3.0. The requisite hydrogen-ion concentration was established by means of a hydrogen phthalate buffer; for the preparation of the latter, solutions of 0.5 M HCl and 0.4 M potassium hydrogen phthalate were used. A pH of 2.2 was obtained by adding 6.25 ml of potassium hydrogen phthalate and 4.7 ml of HCl, and pH of 2.6 by addition of 3.3 ml HCl and 6.25 ml phthalate; a pH of 3.0 was obtained by using 2.03 ml of HCl and 6.25 ml of phthalate; these were the amounts required for the final 50 ml of solution. The amounts of hydrogen phthalate and hydrochloric acid taken correspond to the composition of the buffer mixtures required for these pH values [7].

TABLE 1

Determination of the Composition of the Boric Acid – H-Resorcinol Complex

Vol. H_3BO_3 : : Vol. reagent	Amount, in ml		Optical density	
	H_3BO_3 10^{-3} M	H-resorcinol 10^{-3} M	1st series	2nd series
5 : 1	4,17	0,83	0,232	0,232
4 : 1	4,00	1,00	0,242	0,245
3 : 1	3,75	1,25	0,283	0,290
2 : 1	3,34	1,66	0,350	0,370
1 : 1	2,50	2,50	0,388	0,387
1 : 2	1,66	3,34	0,360	0,370
1 : 3	1,25	3,75	0,280	0,282
1 : 4	1,00	4,00	0,262	0,265
1 : 5	0,83	4,17	0,260	0,260

The dissociation constant K was determined by measuring the light absorption of four series of solutions; the first solution contained 2.5 ml each of the 10^{-3} M solutions of H-resorcinol and boric acid in a total volume of 50 ml. The final concentration of each of the components thus amounted to $(2.5 : 50) \cdot 10^{-3} = 5 \cdot 10^{-5}$ M. The light absorption of this solution was a measure of the amount of the compound formed for a ratio of H-resorcinol to boric acid of 1 : 1. (see Table 1); the first, second and third columns in the table correspond to solutions containing boric acid in amounts which were 20, 40, and 60 times greater than the amount of the acid in the first solution; the amount of H-resorcinol was the same. The value of the light absorption of each of these solutions was found to be proportional to the amount of the compound formed by complete complexing of the components, since in the presence of boric acid the dissociation of the compound should be suppressed. Varying excess amounts of boric acid were taken (20-60 times the amount in the first experiment) for controlling completeness of the suppression of dissociation.

$K_{dissoc.}$ was calculated as follows: from the equation H_3BO_3 + H-resorcinol = B · H-resorcinol.

$$K_{dissoc.} = \frac{(H_3BO_3) \cdot (\text{H-resorcinol})}{(\text{BH-resorcinol})}$$

if one denotes the light absorption of solution 1 with the equilibrium concentration of components by ϵ; while ϵ_{max} denotes the light absorption of a solution in which the dissociation of the complex is suppressed, and the original concentration of the components is $5 \cdot 10^{-5}$ M, then (BH-resorcinol) = $\frac{\epsilon}{\epsilon_{max}} \cdot 5 \cdot 10^{-5}$; $[H_3BO_3]$ = = [H-resorcinol] = $5 \cdot 10^{-5} \cdot \left(1 - \frac{\epsilon}{\epsilon_{max}}\right)$

$$\text{from which } K_{dissoc.} = \frac{5 \cdot 10^{-5}\left(\frac{\epsilon_{max} - \epsilon}{\epsilon_{max}}\right) \cdot \left(\frac{\epsilon_{max} - \epsilon}{\epsilon_{max}}\right)}{\frac{\epsilon}{\epsilon_{max}}} = \frac{(\epsilon_{max} - \epsilon)^2}{(\epsilon_{max} \cdot \epsilon)} \cdot 5 \cdot 10^{-5}.$$

When the degree of dissociation $\frac{\epsilon_{max} - \epsilon}{\epsilon_{max}}$ is denoted by α, then $\frac{\epsilon}{\epsilon_{max}} = 1 - \alpha$, and the equation for the dissociation constant assumes the form:

$$K_{dissoc.} = \frac{\alpha^2}{1 - \alpha} \; 5 \cdot 10^{-5}$$

The experimental values are given in Table 2.

TABLE 2

Determination of the Dissociation Constant of the Compound Formed Between H-Resorcinol and Boric Acid

pH of the solution	Optical density ϵ mean from 3 experiments						
	I 1 : 1 H-resorcinol to H_3BO_3	II 1 : 20	III 1 : 40	IV 1 : 60	Mean II, III, IV ϵ_{max}	α	$K_{dissoc.}$
2,2	0,258	0,739	0,748	0,744	0,744	0,653	$6,15 \cdot 10^{-5}$
2,6	0,259	0,755	0,771	0,766	0,764	0,661	$6,42 \cdot 10^{-5}$
3,0	0,259	0,761	0,771	0,759	0,764	0,661	$6,42 \cdot 10^{-5}$
Mean	0,259	0,752	0,763	0,756	0,757	0,658	$6,33 \cdot 10^{-5}$

Since the value for the light absorption is almost the same for experiments II, III, and IV, thus testifying to suppression of the dissociation constant already at a 20-fold excess of boric acid, it was found possible to take the mean value from the experiments for calculating α. Both the degree of dissociation α, as well as $K_{\text{dissoc.}}$ are independent of pH at 2.2-3.0. Accordingly it was found possible to take the mean value from a series of experiments carried out at various pH's.

Calculation of the molar extinction coefficient was carried out on the basis of the mean value of ϵ_{max} corresponding to complete formation of the compound.

The mean value of ϵ_{max} was 0.757 from which the molar extinction coefficient at 530 mμ was found to be equal to:

$$E = \frac{\epsilon_{\text{max}}^{\text{mean}}}{c \cdot l} = \frac{0.757}{5 \cdot 10^{-5} \cdot 5} = 3028,$$

where c is the concentration in mole/liter; l is the length of the cell in cm.

The values of the molar extinction coefficient in separate experiments were:

$$E_{I} = \frac{0.744}{5 \cdot 10^{-5} \cdot 5} = 2976, \qquad E_{II} = \frac{0.764}{5 \cdot 10^{-5} \cdot 5} = 3056.$$

Conditions for Carrying out the Reaction During the Photometric Determination of Boron. A large excess of H-resorcinol should not be taken, since the solution of the reagent itself exhibits considerable light absorption in the the same wave-length region as that used for measuring the light absorption of the H-resorcinol — boric acid complex (530 mμ). Accordingly, we carried out some tests with the aim of establishing the maximum possible amount of reagent, in the presence of which the light absorption of the complex could be conveniently measured.

TABLE 3

Choice of the Amount of Reagent

Amount of reagent, in ml	Value of the extinction immediately after adding the reagent		Value of the extinction after 24 hours	
	Solution of H-resorcinol and H_3BO_3	Blank test	Solution of H-resorcinol and H_3BO_3	Blank test
2.5	0.316	1.20	0.481	1.21
5.0	0.438	1.73	0.609	1.75
8.0	0.481	2.40	0.653	2.45
10.0	0.629	2.60	0.683	2.68

Solutions were prepared such that 50 ml of the solution contained 2.5 ml of 10^{-3} M H_3BO_3, 5 ml of 1 N acetic acid, and from 2.5 to 10 ml of 10^{-3} M reagent. At the same time experiments were carried out with solutions containing the same amount of all the solutions apart from boric acid.

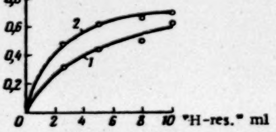


Fig. 2. Relation between the light absorption of solutions containing boric acid, and the amount of reagent.

The light absorption was measured immediately after addition of the reagent, and 24 hours afterwards.

It is evident from the results given in Table 3 that the extinction of the blank even for an amount of reagent equal to 2.5 ml is fairly high (greater than unity) while with increasing amount of reagent, the extinction increases even more. When 5-10 ml of reagent is used, it is so high that the field of vision in the photometer darkens and comparison becomes difficult.

On the other hand, the extinction of solutions containing H_3BO_3 increases with increasing amount of reagent; nevertheless, in the presence of 5-8 ml of reagent, extinctic is weak (Fig. 2).

On this basis an amount of reagent less than 5 ml was chosen, for further work; using this amount of reagent – 4 ml – comparison could still be made quite accurately, while this amount of reagent was also sufficient for ensuring complete formation of the H-resorcinol – boric acid complex.

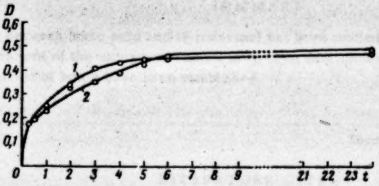


Fig. 3. Relation between color intensity and time of standing of the solution.

In order to establish the length of time for which it is necessary to stand the solution after adding the reagent, for obtaining maximum color intensity, the following experiments were carried out: 2.5 ml of 10^{-3} MH_3BO_3 solution was mixed with 4 ml of 10^{-3} M H-resorcinol and 5 ml of 1 N acetic acid added; the volume was made up to 50 ml. Photometric measurements were made $^1/_4$, $^1/_2$, 1, 2, 3, 4, 5, 6, and 24 hours after mixing the reagents, using the conditions described above.

TABLE 4

Relation Between Light Absorption of the Solution and Amount of Boron

Boron content, in γ	Light absorption of the solution
1.1	0.086
2.2	0.088
5.5	0.151
11.0	0.249
16.5	0.289
22.0	0.366
27.5	0.398
44.0	0.551
66.0	0.634

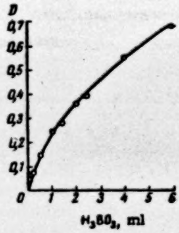


Fig. 4. Relation between the color intensity of the solution and the boron content.

Measurements were carried out both on solutions kept at room temperature, and on solutions which had been heated almost to the boiling point on addition of the reagents and then cooled under tap water.

As the results shown in Fig. 3 demonstrate, the curves already coincide within the course of the first 4-6 hours after addition of reagent, while the further increase in color or light absorption of the solution is insignificant. Accordingly, the colored solution should be allowed to stand for 4-6 hours. Heating of the solution does not seem to be obligatory, since the curves obtained with and without heating coincide.

In order to establish the relation between color intensity and the boron content, a series of solutions were prepared containing from 0.1 to 6.0 ml of 10^{-3} M boron (from 1.1 γ to 66 γ B). 4 ml of reagent was added, followed by 5 ml of 1 N acetic acid, and the volume made up to the mark with water. The light absorption was measured against a blank after 20 hours.

As the results given in Table 4 and Fig. 4 show, the relationship between boron concentration and light absorption is non-linear; consequently, when determining boron by this method it is necessary to construct a calibration curve on the basis of several points.

As a result of all the experiments carried out, the following conditions have been chosen for determining boron by means of H-resorcinol; for amounts of boron from 1.1 γ to 66.0 γ, 4 ml of reagent should be taken (10^{-3} M), together with 5 ml of 1 N acetic acid, and the total volume made up to 50 ml. The color almost reaches its maximum intensity after 4-6 hours and thereafter does not increase appreciably. The relationship between color intensity and boron concentration is curvilinear within these limits.

SUMMARY

The interaction between boric acid and H-resorcinol has been studied. The dissociation constant and the molar extinction coefficient of the compound formed have been determined. The optimum conditions for the photometric determination of boron have been established.

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PHOTOMETRIC DETERMINATION OF GALLIUM BY MEANS OF GALLION

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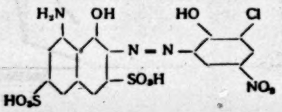
8-Hydroxyquinoline has been used for the photometric determination of gallium [1, 3], as well as quinalizarin [3, 2] which is of low selectivity, and aluminon which shows low sensitivity and forms with gallium, just like quinalizarin, a bright-red colored lake [4]. Recently, rhodamine B [5] has found wide use in the fluorescent determination of gallium. Lukin and Zavarikhina [6] have shown that the product obtained by coupling H-acid with the diazo compound from 2-amino-4-nitro-6-chlorophenol, and arbitrarily called gallion, is an interesting reagent for gallium.



2-hydroxy-3-chloro-5-nitrobenzene-
-(1-azo-2)-1'-hydroxy-8'-alinonaphthalene-
-3',6'-disulfonic acid.

Gallion is a dark-red powder which is soluble in water; a 0.01% transparent aqueous solution has a dark-red color, acid aqueous solutions are bright-red in color [6], while alkaline solutions are violet-blue. The reagent is readily soluble in ethyl and isoamyl alcohols, and also in acetone; it is sparingly soluble in chloroform and dichloroethane. A solution of the reagent forms, at varying pH values, colored compounds with various elements. An aqueous solution of the reagent forms, with gallium, a blue-colored compound.

TABLE 1

Interaction of Metal Ions with Gallion

Element	pH	Color	
		Peagent solution	Compound of element and reagent
Co	4,2—5,6	Rose-violet	Violet
Ni	4,2—5,6	»	Blue-violet
Al	3,2—5,6	»	Blue
Mn	3,4—6,3	»	Violet
Ti	2,0—4,6	»	Blue-violet
Fe^{3+}	2,2—5,6	»	»
Bi	8.5—11	Violet-blue	»
Cr^{III}	9,2—11	»	»
Th	2,4—3,6	Violet-rose	Violet
In	3,2—4,4	Rose-violet	Blue
Ce	2,4—3,8	»	»
Cu	2,2—5,6	»	Violet
Sc	2,2—4,2	»	Blue
Ga	2,2—4,8	»	Pale blue

Gallion changes its color from red to blue-violet in the pH range 3.8-5.8. Above 5.8, the violet-blue color does not change until a pH of 13 is reached. On increasing the pH further, the color starts to change; it first acquires a rose color, and then at pH about 14, the solution has the same color as at pH 4.0 (Fig. 1).

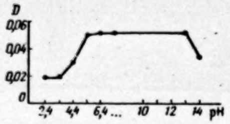


Fig. 1. Change of the color of gallion solutions with pH.

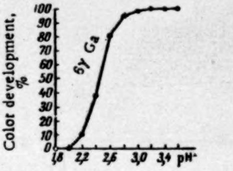


Fig. 2. Intensity of the color of gallion solutions as a function of pH.

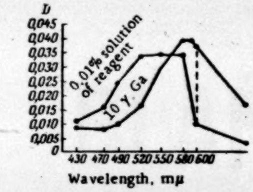


Fig. 3. Determination of the maximum light absorption for the compound formed between gallion and gallium (10 γ of Ga in 10 ml).

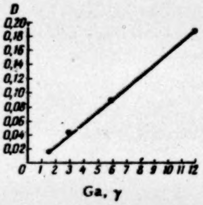


Fig. 4. Relation between optical density and gallium concentration.

The optimum pH range for gallium determination is 2.4-3.4 (Fig. 2). Maximum light absorption is observed at 600 mμ (Fig. 3). For the determination of gallium, it is convenient to use a hydrogen phthalate buffer, although the latter is sensitive to temperature changes, particularly at pH 2.4. When the temperature drops (down to +16°) crystals are deposited.

When optimum conditions are used for determination of gallium (pH of about 3.2), the sensitivity of the reaction amounts to 0.2 γ of Ga in 5 ml of solution.

Conditions used for Gallium Determination. To 2 ml lots of solution containing 0.2, 0.5, 1, 2, 4, 6, 8, and 12 γ of Ga, and 2 ml of water (control) contained in test tubes, was added a hydrogen phthalate buffer with a pH of about 3.2* until the volume was 4.5 ml, when 0.5 ml of a 0.01% aqueous solution of gallion was added. The color developed in the first minute, and was complete in 10-15 minutes. The temperature strongly affects development of the color. Thus, on heating to 60-100°, complete color development is achieved in 1½ - 2 minutes. After cooling, the scale is stable for 40 hours (Table 2). The relationship between color intensity and gallium concentration of the solution is linear (Fig. 4). By heating, it is possible to determine gallium by the method of colorimetric micro-titration. For this purpose, 1 ml of a weakly acid (pH about 2-2.6) or neutral test solution, containing from 0.5 to 12 γ of Ga, was introduced into a test tube, and buffer solution (pH about 3.2) added to bring the volume up to 4.6 ml, 0.4 ml of a 0.01% aqueous solution of gallion was then added. At the same time, into another test tube was introduced 4.6 ml of the same buffer solution and 0.4 ml of gallion solution. Both tubes were immersed in a beaker containing hot water kept constant at about 85°. To the test tube not containing the gallium was then added from a buret, carefully, and in small portions, a standard solution of gallium containing 2.5 γ of Ga per ml; towards the end point the solution was added dropwise, until the colors of the test solution and standard solution were the same. Results of such a titration are given in Table 3.

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* The hydrogen phthalate buffer was prepared by mixing 25 ml of a 0.2 M solution of potassium hydrogen phthalate with 7.35 ml of 0.2 M hydrochloric acid and 67.65 ml of water.

TABLE 2

Stability of the Color of the Gallium Compound at pH about 3.2

Ga taken, in γ	Optical density			
	after 5 min	after 1 hr	after 18 hr	after 40 hr
0,6	0,0018	0,0018	0,0016	0,0016
1,2	0,0027	0,0027	0,0026	0,0026
2,4	0,0052	0,0052	0,0051	0,0052
4,8	0,0109	0,0108	0,0109	0,0109
9,6	0,0230	0,033	0,025	0,0230

TABLE 3

Determination of Gallium by Colorimetric Microtitration.

Ga taken, in γ	Ga found, in γ	Relative error, in %	Ga taken, in γ	Ga found, in γ	Relative error, in %
1,1	1,12	+ 2	7,8	7,85	+0,6
1,7	1,7	0	11,8	11,82	+0,2
2,5	2,52	+0,8	1,50	1,50	0
3,5	3,55	+1,4	2,25	2,25	0
5,2	5,2	+0,9	—	—	—

TABLE 4

Determination of Gallium in the Presence of Other Elements at pH about 3.2.

Gallium		Error, in γ	Me, in γ	Ratio Ga : Me	Gallium		Error in γ	Me, in γ	Ratio Ga : Me
intrd. in γ	found in γ				intrd. in γ	found in γ			
0,5	0,5	0	Ge 300	1:600	1,0	1,3	+0,3		
2,0	2,0				2,0	2,2	+0,2	In 300	1:15
0,5	0,55	+0,05	Pr 100	1:200	2,0	2,1	+0,1	Rh 30	1:15
2,0	2,1	+0,1			1,0	1,1	+0,1	Tl 1000	1:1000
0,5	0,5	0	La 100	1:200	1,0	1,0	0	Re 100	1:100
2,0	1,8	—0,2			4,0	3,8	—0,2		
0,5	0,5	0	Mn 200	1:400	1,0	1,0	0	Pb 100	1:100
1,0	1,1	+0,1			2,0	2,0	0		
2,0	1,8	—0,2	Co 100	1:200	0,5	0,55	+0,05	Mg 50	1:100
0,5	0,55	+0,05			2,0	1,8	—0,2		
4,0	4,0	0	Zn 200	1:400	0,5	0,5	0	Ca 100	1:200
0,5	0,5	0			1,0	1,0	0	Be 50	1:50
0,5	0,4	—0,1	Li 100	1:200	1,0	1,0	0	In 50*	1:50
1,0	1,1	+0,1			1,0	1,0	0	Al 50*	1:50

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* Ga was determined in the presence of aluminum and indium at a pH of 2.4.

In Table 4 are given the limiting ratios of gallium to other metals which do not form colored compounds with gallion (Ge, La, Pr, Rh, Te, Tl, Pt, Zn, Hg^{2+}, Ir, Be, Cd, Pb, Ca and Mg), at which gallium can still be determined with permissible accuracy. Aluminum and indium form colored compounds with gallion at a pH of about 3.2. Nevertheless, in more acid media (pH about 2.4) we were able to determine gallium in the presence of these elements at a ratio of Ga : Al = 1 : 50 and of Ga : In = 1 : 50 (Table 4).

TABLE 5

Determination of Gallium after its Extraction by Isoamyl Alcohol from a Solution Containing Other Elements

Me taken, in γ	Gallium		Relative error, in %
	introduced, in γ	found, in γ	
Al 1000	0.5	0.5	0
Fe^{3+} 250	1.0	0.9	−10
Cu^{2+} 200	1.0	1.0	0
	2.0	1.85	−8
	1.0	1.2	+ 20
Al 1000	2.0	1.8	−10
Cu 250	2.0	2.25	+ 12
In 200	2.0	2.15	+ 7
	1.0	1.15	+ 15

Fe^{3+} and Cu^{2+} ions strongly interfere with determination of gallium, but at contents of these elements not greater than 50 γ, iron can be reduced by addition of 0.5 ml of a freshly prepared 20% solution of hydroxylamine hydrochloride, while copper can be reduced by addition of 0.25 ml of 0.1 N sodium thiosulfate. After addition of hydroxylamine, excess acid is neutralized with a 2% solution of sodium acetate to a pH of about 2.4-3.2.

TABLE 6

Determination of Gallium after its Extraction with Amyl Acetate from Salts and Minerals*

Natrolite $Na_2(Al_2Si_3O_{10})\cdot 2H_2O$		Relative error, in %	$K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$		Relative error, in %	$Al_2(SO_4)_3$		Relative error, in %	Amazonite $K(AlSi_3O_8)$		Relative error, in %
Ga intrd. in γ	Ga found		Ga intrd, in γ	Ga found, in γ		Ga intrd, in γ	Ga found, in γ		Ga intrd. in γ	Ga found in γ	
—	1,8	—		Not detected	—	—	Not detected	—	—	1,6	—
1,0	2,9	+4	1,0	1,1	10	1,0	1,0	0	2,0	3,8	+5
1,0	2,8	0	1,0	1,0	0	1,0	1,2	+20	2,0	3,5	−3
1,0	3,0	+7	1,0	1,15	+15	1,0	1,1	+10	4,0	5,4	−4
2,0	3,8	0	2,0	1,9	−5	2,0	2.2	+10			
2,0	3,7	−3	2,0	2,2	+10	2,0	2,1	+5			
0,5	2,2	−5									
0,5	2,25	−3									

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* Determination was carried out on 5 ml of test solution; total volume 10 ml.

As the results given in Table 4 show, zinc, aluminum, and indium, in small amounts, do not interfere with determination of gallium; large amounts of these elements, however, distort the results for gallium determination. Accordingly, during analysis of aluminosilicates, aluminum alloys, zinc blendes and other materials, where traces of gallium are present, it is necessary to separate the gallium.

Usually, gallium is extracted from interfering elements by extraction with an organic solvent from a hydrochloric acid solution [5, 7]. Use is made of the extraction of gallium by ethyl ether from 6 N hydrochloric acid solution [3]. The ether extracts are evaporated and gallium determined in the residue. Gallium can also be extracted with isopropyl ether [5]. Bearing in mind the high volatility and ready inflammability of ether, we thought it best to extract gallium with isoamyl alcohol and ethyl acetate from a 6 N hydrochloric acid solution. Hydroxylamine is added to the solution containing gallium and the other elements in order to reduce Fe^{3+}, while thiosulfate is added to reduce Cu^{2+}.

TABLE 7

Determination of Gallium in Minerals and Metallic Aluminum

Sample	Gallium found by means of gallion, in %	Gallium found by means of quinalizarin, in %
Natrolite $Na_2(Al_2Si_3O_{10}) \cdot \cdot 2H_2O$	0.018	0.02
Amazonite $K(AlSi_3O_8)$	0.016	0.016
Metallic alluminum	Not detected	Not detected

Procedure for Removal and Determination of Gallium. When the test alloy or mineral is soluble in hydrochloric acid, 0.1 g of sample (weighed out to an accuracy of 0.001 g) is dissolved in 10 ml of hydrochloric acid 1 : 1, and the solution transferred to a separating funnel. The vessel in which the sample is dissolved is carefully washed out with 3 lots of 3 ml of the same hydrochloric acid. To the final solution in the separating funnel is added 3 ml of 20% freshly prepared hydroxylamine hydrochloride solution, 0.25 ml of 0.1 N sodium thiosulfate and (for keeping the acid concentration at 1 : 1) 3.25 ml of concentrated hydrochloric acid (sp. gr. 1.18-1.19). 5-8 ml of amylacetate or isoamyl alcohol is then added and the whole shaken for 1.5-2 minutes, after which the layer of amyl acetate or isoamyl alcohol is transferred to another separating funnel. Extraction is repeated twice again, each time with 5 ml of the organic solvent chosen. The combined extracts are washed three times with hydrochloric acid 1 : 1, containing in each portion of wash liquor 1 ml of 20% hydroxylamine hydrochloride, 0.25 ml of sodium thiosulfate, and 1.25 ml of concentrated hydrochloric acid; washing is carried out with 2-3 ml each time. The washed extract is neutralized in the separating funnel with 2.5% ammonia solution; excess ammonia is added (1-2 ml) and the whole shaken for $1^1/_2$-2 minutes; the aqueous phase is transferred to a 25-50 ml standard flask. The operation of transferring gallium into the aqueous phase with ammonia is repeated twice again. The aqueous-ammonia layers are added to the same standard flask. The solution in this flask is carefully neutralized with hydrochloric acid 1 : 1, and one drop of acid added in excess. The volume of the solution is made up to the mark with a buffer solution having a pH of about 3.2. Before determining the gallium it is necessary to check the pH of the solution. For this purpose 1-2 ml of the test solution is introduced into a test tube and the volume made up to 5 ml with buffer solution. Into a second test tube is introduced 5 ml of the same buffer solution with an accurately established pH (potentiometrically or otherwise). An equal amount of methyl orange (1-2 drops each) is added to each tube; the color should be the same in both cases. If the test solution should prove to be more acid than it should be, 2% sodium acetate solution is added until the color of the test solution is the same as that of the buffer solution. If, on the other hand, it should prove to be too alkaline, then 0.1 N hydrochloric acid is added. The amount of sodium acetate or 0.1 N hydrochloric acid established is only added to the test solution. The scale is prepared over the range 0.5-12 γ Ga; buffer solution (pH about 3.2) is then added to bring the volume up to 4.5 ml, and 0.5 ml of a 0.01% aqueous solution of gallion added to each. The test solution and the series of standard solutions forming the scale, contained in test tubes, are immersed in a vessel with boiling water for 1.5-2 minutes, and then cooled and the colors compared.

In those cases where the mineral does not dissolve in hydrochloric acid, it is fused and the melt dissolved in HCl.

Using the conditions described, gallium was determined in synthetic mixtures, and also in metallic aluminum, aluminum-potassium alum, in aluminum salts and in the minerals natrolite and amazonite. The results obtained are given in Tables 5-7.

SUMMARY

The product formed by coupling H-acid with the diazo compound from 2-amino-4-nitro-6-chlorophenol reacts with gallium to form a colored compound at a pH of 2.4-3.2 which is stable for 40 hours. The sensitivity of the reaction is 0.2 γ of Ga in 5 ml of solution.

A method is described for the determination of gallium in various test materials.

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DETERMINATION OF INDIUM PRESENT AS AN IMPURITY IN GERMANIUM

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The photometric methods which are known for the determination of indium – those based on 8-hydroxyquinoline or morine – are not specific enough. In the presence of various masking agents, added in order to enhance the specificity, the sensitivity of these methods decreases appreciably. A method described recently for the determination of indium as an impurity in germanium by means of 8-hydroxyquinoline [1], permits determination of indium down to $1 \cdot 10^{-4}$%, but this is not always low enough.

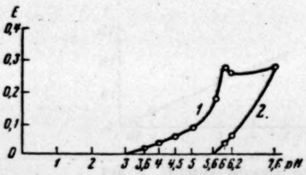

Fig. 1. Effect of pH on color development: 1) Indium complex; 2) reagent.

With the aim of finding a more sensitive, and reasonably specific method for determining indium as as impurity in germanium, we tested various color reactions for the former. Of the color reactions tested, the one that proved most convenient for quantitative determination was the reaction with diphenylcarbazone described by Poluektov and N. K. Kiseleva [2].

Diphenylcarbazone as a Reagent for Indium. Diphenylcarbazone in a very weakly acid medium (pH < 7) gives a violet color with indium; when large amounts of indium are present, a violet precipitate is formed. When no indium is present the solution remains a brownish-yellow color. The relation between the color intensity and pH of the solution is shown in Fig. 1.

Tests were carried out as follows: to 1 ml of a neutral solution of indium chloride (5 γ of In) were added 0.5 ml of a 0.1% solution of diphenylcarbazone and 4 ml of an appropriate buffer solution. The optical density was measured 5 minutes afterwards on a Pulfrich photometer using a 10 mm cell; the wave-length used was 570 mμ while water served as the reference solution. A blank was carried out under the same conditions, indium being omitted. It is evident, from the Fig. that the optimum pH of the solution is 6 (hydrogen phthalate buffer).

At pH 5-6, 50 γ of each of the following elements does not react with diphenylcarbazone: magnesium, calcium, aluminum, chromium, (III), tin (IV), antimony, arsenic, silver, germanium, and thallium. Copper (II) and zinc behave like indium. Gallium also reacts, but the reaction sensitivity is considerably less in this case than for indium. Iron (III) exhibits a characteristic behavior; while it does not itself react with diphenylcarbazone under the conditions used, it almost completely masks indium, presumably as the result of trapping of indium by the precipitate of ferric hydroxide formed during hydrolysis at the high pH of the solution. Even as little as 2 γ of iron halves the color intensity resulting from 5 γ of indium.

It was found possible to eliminate interference from iron by using thiourea; nevertheless this could only be done at pH 5.6 (hydrochloric-pyridine buffer). No method of masking iron could be devised when the pH was 6 (hydrogen phthalate buffer). The use of a reducing agent (ascorbic acid, thioglycollic acid) for converting iron into the divalent state was not possible in this instance because of the reduction of diphenylcarbazone to carbazide, which does not react with indium. Other complexing agents hydroxycarboxylic acids, cyanide) mask indium as well as iron. In the presence of acetylacetone, iron fluoride reacts with diphenylcarbazone.

Thiourea, in addition to masking iron, also masks copper and weakens the reaction with zinc.

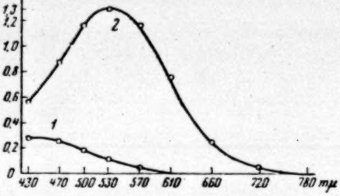

Fig. 2. Absorption curves: 1) Reagent; 2) reagent + indium.

Because of the necessity of eliminating interference from iron, it was found best to determine indium at a pH of 5.6. At this pH the color intensity, as is evident from Fig. 1, is half of that at pH 6; nevertheless the reaction gains in specificity.

Absorption curves for the reagent itself and for the indium-reagent complex are shown in Fig. 2. The solutions used were prepared as indicated above, but the indium was taken in excess with respect to the reagent (25 γ). The buffer was a hydrochloric-pyridine mixture with a pH of 5.6. It follows from Fig. 2 that the absorption maximum of the indium complex lies at 530 mμ; at this wave-length, however, absorption by the reagent itself is discernible. It is more convenient, therefore, to determine indium at 570 mμ, where the reagent itself does not absorb, while the absorption exhibited by the complex is only slightly less than the maximum absorption.

Within the limits 0.4-5 γ, solutions of indium conform to the Beer law (Fig. 3).

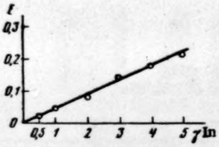

Fig. 3. Relation between color intensity and amount of indium.

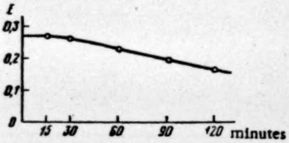

Fig. 4. Effect of time on color development.

In these experiments, thiourea (0.5 ml of a 10% solution) was added to the reaction solutions. The buffer was a hydrochloric–pyridine mixture with a pH of 5.6. Optical density was measured in a Pulfrich photometer at 570 mμ. Measurements can also be made on a FEK-M photocolorimeter, but in this case it is necessary to use a combined filter (green and orange glass).

It can be seen from Fig. 4 that the color is stable for less than 15 minutes; at the end of this time it gradually weakens, mainly because of coagulation of the complex. Accordingly, all measurements should be carried out not later than 10 minutes after preparing the solutions.

Determination of Indium in Germanium. Determination of micro amounts of indium in germanium is possible after removal of germanium by distillation in the form of its tetrachloride. All the indium remains in the residue; this fact was checked by means of the radioisotope In^{114}.

During the analysis of pure germanium dioxide, using purified reagents, the indium can be determined directly in the residue after removal of germanium. When, however, impure germanium dioxide is analyzed, or metallic germanium, the residue may contain interfering metals, mainly iron. In such cases, it is necessary to separate the indium; this is readily carried out by extraction from hydrobromic acid with ether. In order to prevent iron from passing into the extract at the same time, extraction is carried out in the presence of titanium trichloride.

The use of a hydrochloric–pyridine buffer, which has a comparatively low capacity for the determination of indium, demands that the test solution be neutralized as far as possible. During evaporation of acid solutions to dryness, hydrolysis of indium salts is observed and this can lead to low results. Addition of a small amount of sodium chloride to the indium solution prior to evaporation prevents hydrolysis, because of the formation of sodium chloroindiate. Sodium chloride does not subsequently interfere with indium determination.

Reagents. Concentrated hydrochloric acid. This is obtained by saturating twice-distilled water with hydrogen chloride in a quartz vessel.

2. Nitric acid, concentrated, purified by distillation in a quartz apparatus.

3. Hydrobromic acid, 5 N, saturated with ether. The commercial acid is purified by distillation in a quartz apparatus and diluted with water to the requisite concentration. This 5 N solution is saturated with ether by shaking it in a separating funnel with an equal volume of ether free from peroxides, and, after separating into two layers, keeping the two phases separately.

4. Peroxide-free diethyl ether. The ether is purified by distillation after standing over sodium metal. The distilled ether is saturated with hydrobromic acid.

5. Sodium chloride, 1% solution.

6. Titanium trichloride, 20% solution in 6 N hydrochloric acid.

7. Thiourea, 10% solution.

8. Pyridine buffer. To 98 ml of 0.01 N hydrochloric acid is added 2 ml of a 10% solution of pyridine. The pyridine is purified by distillation over sodium hydroxide.

9. Diphenylcarbazone, 0.1% solution in 96% ethanol.

TABLE 1

Determination of Indium in the Absence of Germanium, Complete Analysis

In taken, in γ	In found, in γ	Difference, in γ
0.5	0.5	−0.1
1.0	1.1	+ 0.1
2.0	2.0	0
4.0	4.0	0
5.0	4.9	−0.1

Calibration Curve. Into quartz crucibles is measured standard indium solution (5 γ per ml) in amounts corresponding to 0.5, 1, 2, 3, 4, and 5 γ of In; one crucible is left empty (for the blank). Water is added to each crucible to bring the volume up to 1 ml; 0.2 ml of sodium chloride and 0.5 ml of hydrochloric acid is then added to each crucible; the contents of each crucible is then treated as follows. It is evaporated to dryness on a water bath and the residue moistened with 1 ml of water, the water is used for washing down the sides of the crucible, after which it is evaporated to dryness again. The dry residue is transferred to a test tube using 1.5 ml of water; 0.5 ml of thiourea solution, 0.5 ml of diphenylcarbazone and 2.5 ml of the pyridine buffer are added to each; the liquid is mixed after addition of each reagent. After 5 minutes the optical density of the solution is measured using a 10 mm cell against the blank solution; the wave length used is 570 mμ; measurements can be made either on a photometer, or on a photocolorimeter with a double filter (green and orange). A calibration curve is constructed on the basis of the results obtained.

TABLE 2

Determination of Indium added to 2 g of GeO_2, without Ether Extraction

In added		In found		Difference	
in γ	in % $\times 10^5$	in γ	in % $\times 10^5$	in γ	in % $\times 10^5$
0	0	0	0	—	—
0,5	2,5	0,47	2,4	−0,03	−0,1
1	5	1	5	0	0
1	5	1,1	5,5	+0,1	+0,5
3	15	3,1	15,5	+0,1	+0,5
3	15	2,9	14,5	−0,1	−0,5
4	20	3,8	19	−0,2	−1

TABLE 3

Determination of Indium added to Metallic Germanium; (complete analysis)

Weight of Ge, in g	In added		In found		Difference	
	in γ	in % $\times 10^5$	in γ	in % $\times 10^5$	in γ	in % $\times 10^5$
2	0	0	0	0	—	—
2	0,5	2,5	0,5	2,5	0	0
2	1	5	0,8	4	−0,2	−1
1	1	10	1	10	0	0
1	3	30	3	30	0	0
1	4	40	3,8	38	−0,2	−2
1	5	50	5	50	0	0

Determination of Indium. 1-2 g of coarse germanium powder is carefully heated in a quartz flask with

10 ml of 12 N hydrochloric acid and 2 ml of nitric acid; the heating, which is carried out on a sand bath, is continued until the volume is 2-3 ml. 10 ml of hydrochloric acid and 2 ml of nitric acid are added again, and the whole heated until all the metal particles have dissolved. Where necessary, the residue should be given a thrid treatment with addition of acid. The acids are finally evaporated until a residue of about 1 ml remains.

During the analysis of germanium dioxide, 2 g of sample is placed in a quartz flask and 20 ml of 8 N hydrochloric acid added; the mixture is evaporated until a volume of about 1 ml remains in the flask. Germanium may be separated from the collected distillates.

After dissolution, and removal of germanium by distillation, the residue in the flask is washed into a quartz crucible with the aid of 5 ml of water; 0.2 ml of sodium chloride solution is added and the mixture evaporated to dryness on a water bath. The residue is dissolved in 5 ml of hydrobromic acid and transferred to a separating funnel, 0.1 ml of titranium trichloride is added, and the solution extracted three times with 3 ml lots of ether. Shaking is carried out for one minute each time. The combined extracts are washed 3 times with 3 ml lots of hydrobromic acid. The washed extracts are poured into a quartz crucible, and 0.2 ml of sodium chloride solution and 0.5 ml of 6 N hydrochloric acid added; the mixture is then evaporated to dryness, first on a warm bath, and finally on a boiling water bath. The residue is moistened with water, the water being added so as to wash down the walls, and the whole evaporated to dryness once again. The residue is finally washed into a test tube by means of 1.5 ml of water. The procedure subsequently followed is the same as that described for construction of a calibration curve. Measurements are made against a blank solution (the same solution, but without indium).

Compact germanium is ground up in an agate mortar between layers of white cotton fabric. Compact germanium can also be brought into solution by anode dissolution [3].

As the results given in Tables 1-3 show, the method gives satisfactory results. When 2 g of germanium or its dioxide is taken for analysis, it is possible to determine as little as 0.4 γ of In: this corresponds to $2 \cdot 10^{-5}$%. From the point of view of simplicity and specificity, the method is applicable to the analysis of germanium for its indium content, with the sensitivity indicated.

SUMMARY

A method for the photometric determination of indium, based on the use of diphenylcarbazone, has been developed. The method permits determination of 0.4 γ of In in 5 ml of solution. The method is applicable to the determination of indium present as impurity in metallic germanium and germanium dioxide; the sensitivity is $2 \cdot 10^{-5}$%.

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**In Russian.

APPLICATION OF THE METHOD OF ADDITIONS DURING TITRIMETRIC DETERMINATION OF BISMUTH

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Of the known titrimetric methods of determining bismuth [1] the most promising would appear to be the phosphate method, although, without exception, all the variants of the titrimetric method hitherto suggested possess poor reproducibility and are not accurate enough. The hardly appreciable solubility of the precipitate of $BiPO_4$ in dilute nitric acid, the rapid formation of a heavy crystalline precipitate, etc., however, do open up prospects of using the formation of $BiPO_4$ as a method for the titrimetric determination of Bi. The reason for the lack of success hitherto can be attributed to the absence of satisfactory indicators for clearly establishing the equivalence point.

The method consists of precipitating bismuth from nitric acid solution in the presence of sodium acetate, using excess of a standard solution of sodium phosphate. After filtering off and washing the precipitated $BiPO_4$, the excess sodium phosphate is titrated with standard uranyl acetate. The equivalence point is established by an external indicator – potassium ferrocyanide. Other research workers [2] have titrated the excess phosphoric acid with uranyl acetate, and determined the equivalence point with an external indicator (tincture of cochineal). A method even more complicated [3] is addition of excess standard Na_2HPO_4 solution to a boiling sample of the bismuth nitrate solution. The $BiPO_4$ precipitate formed is then filtered off and washed, and the filtrate plus washings transferred to a standard flask in which it is neutralized with sodium hydroxide; 50 ml of 0.1 N sodium acetate is then added followed by 50 ml of standard $AgNO_3$ and the volume of the solution made up to 500 ml. An aliquot of this solution plus excess $AgNO_3$ is finally titrated by the Volhard method. This method, as a consequence of the numerous operations involved, which lead to appreciable losses, does not give reliable results.

TABLE 1

Determination of Bismuth by the Ehrenfeld, Krause, and Addition Methods Respectively

Bi taken, in g	Bi found					
	Ehrenfeld method		Krause method		Addition method	
	in g	Error, in %	in g	Error, in %	in g	Error, in %
0,050	0,046	−8,0	0,048	−4,0	0,0505	+1,0
0,050	0,047	−6,0	0,052	+4,0	0,0500	+0,0
0,080	0,075	−6,3	0,076	−5,0	0,0805	±0,63
0,080	0,085	+6,3	0,083	+3,7	0,798	−0,25
0,120	0,125	+4,2	0,124	+3,3	0,121	+0,83
0,120	0,115	−4,2	0,115	− 4,2	0,120	±0,0
0,160	0,170	+6,3	0,165	+3,1	0,1615	±0,94
0,160	0,155	−3,2	0,153	− 4,4	0,1610	+0,63

A simpler method [4] involving direct titration with standard Na_2HPO_4 neutralized with ammonia, of the bismuth solution acidified with a few drops of nitric acid, does not give any better results. The equivalence point is established by the change in color of haematin indicator paper. In our experiments the experimental error of this method varied from + 7.0 to + 9.0% during determination of from 0.04 to 0.1 g of Bi.

The method of additions, which is applicable in this case, gave satisfactory results (Table 1).

TABLE 2

Dependence of the Degree of Oxidation of Metallic Bismuth (0.178 g) on the Concentration of $FeCl_3$

$FeCl_3$ solution added, in ml	Amount of Fe^{3+} participating in the reaction, in g/ion	By the usual method			By the addition method		
		$KMnO_4$ solution used, in ml	Bi found, in g	Error, in %	$KMnO_4$ solution used, in ml	Bi found, in g	Error, in %
8.0	0.248	21.2	0.162	−8.7	22.10	0.1690	−5.0
10.0	0.356	22.1	0.169	−5.0	22.80	0.1755	−1.4
12.0	0.427	22.4	0.172	−3.4	22.83	0.1760	−1.1
15.0	0.533	22.7	0.174	−2.0	23.0	0.1770	−0.6

Of the methods based on preliminary reduction of bismuth ions to the metallic state by means of magnesium, zinc, copper [5], aluminum [6], and other metals, with subsequent oxidation of bismuth metal with ferric chloride, the most simple, rapid, and accurate method is the one involving reduction with aluminum dust.

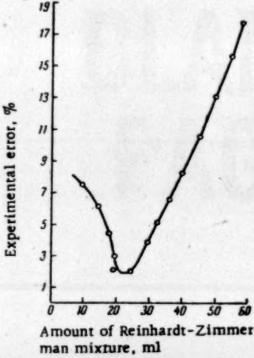

Fig. 1. Relationship between the accuracy of titration of ferric chloride solution and the amount of Reinhardt--Zimmerman mixture.

We have studied the kinetics of the reduction of bismuth, and the effect of ferric chloride concentration on the oxidation of bismuth metals, and have established the optimum amounts of the Reinhardt-Zimmerman mixture that should be added.

For the determination of bismuth a weakly acid solution containing up to 0.25 g of bismuth was mixed with 0.1 g of freshly prepared aluminum dust or copper turnings, and the mixture allowed to react for 15 minutes after addition of the reagents and shaking. 40 ml of 5% potassium hydroxide was added and the whole boiled until all the aluminum had dissolved; the mixture was then diluted with distilled water and the precipitate decanted through a filter; the spongy, metallic deposit of bismuth was filtered and washed with warm distilled water, and treated with 15 ml of ferric chloride solution (200 g of $FeCl_3$, 250 ml of concentrated HCl, and the volume made up to 1 liter with distilled water). To this mixture was added the Reinhardt-Zimmerman mixture; the whole was then greatly diluted, and the ferrous ions formed as the result of oxidation of metallic bismuth titrated with 0.1 N $KMnO_4$.

The relationship between the degree of oxidation of metallic bismuth and the amount of $FeCl_3$ is shown in Table 2.

During titration of $FeCl_3$ solution with permanganate, Reinhardt-Zimmerman (20 ml) was added to the solution being titrated. During oxidation of 0.25 g of Bi, the optimum amount of $FeCl_3$ used should amount to not less than three equivalents per equivalent of bismuth. On increasing the amount of $FeCl_3$ beyond this amount, the experimental error increases rapidly. Even under optimum conditions, however, when the usual method is used, the experimental error is high; it amounts to 2 to 3%. When the method of additions is used, the error drops to 1.4 to 0.6%.

During titration of divalent iron with permanganate in the presence of chloride ions, induced oxidation of Cl^- occurs. In order to prevent oxidation of chloride ions, various amounts of Reinhardt-Zimmerman mixture are added to the liquid being titrated. When this technique has been used,previously, various authors have obtained conflicting results. We studied the effect of the amount of this mixture on the accuracy and reproducibility of $FeCl_2$ determination, and established (Fig. 1) that the best results are obtained when 20-25 ml of this mixture is taken per 10 ml of iron chloride solution. On decreasing or increasing this amount of the mixture, the error increases sharply.

Rupp [6] established that Fe^{2+} in the presence of excess phosphoric acid is oxidized very slowly, presumably as the result of the formation of fairly stable ferrous—phosphate complexes [7-9] of the type $H_4[Fe(PO_4)_2]$ and $H_7[Fe(PO_4)_3]$ etc. Accordingly, on addition of large amounts of Reinhardt-Zimmerman mixture, titration of iron gives a considerable negative error.

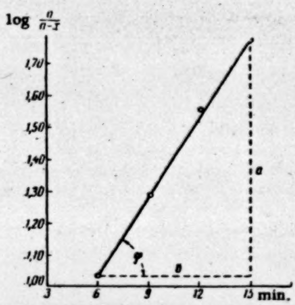

Fig. 2. Kinetics of the reduction of bismuth by metallic aluminum: a) Initial bismuth concentration; a - x) its concentration after time t.

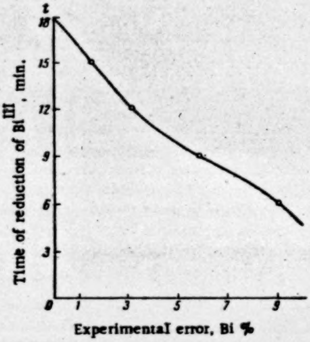

Fig. 3. Experimental error in the determination of bismuth as a function of the duration of reduction with metallic aluminum.

Results of a study of the kinetics of the reduction of bismuth by metallic aluminum at 40° are given in Fig. 2. In this case, a function of the formula given below is observed.

$$K = \frac{1}{t} \lg \frac{a}{a - x}.$$

K = 0.125 at 40°. Bismuth is reduced almost completely after 18 minutes (Fig. 3).

SUMMARY

1. It has been shown that the method of additions, when applied to the titrimetric determination of bismuth, leads to increased accuracy and reproducibility of the results.

2. The best titrimetric method of determining bismuth is the one involving its preliminary reduction with metallic aluminum followed by oxidation of the reduced bismuth with excess ferric chloride.

3. The optimum conditions have been established for oxidation of metallic bismtuh with ferric chloride solution.

Received October 29, 1956

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ORGANIC COPRECIPITANTS

COMMUNICATION 9. CONCENTRATION AND SPECTROGRAPHIC DETERMINATION OF MOLYBDENUM IN NATURAL WATERS*

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The presence of molybdenum in natural waters can serve as a prospecting sign for molybdenum, tungsten, and also certain types of copper and cobalt deposits. In natural waters which are found outside the influence of ore deposits, and which have a mineral content of up to 1-2 g/liter, the molybdenum content, usually, does not exceed 10^{-7}-10^{-6} g/liter. Near ore bodies containing molybdenum, the molybdenum content may increase to 10^{-4}-10^{-3} g/liter, for waters with the mineral content indicated above [1]. For the determination of molybdenum at this concentration in natural waters it is necessary to use highly sensitive methods, the most important of which is the spectrographic method.

Nevertheless, the amount of molybdenum and other micro elements in natural water is usually below the sensitivity of the spectrographic method; accordingly spectrographic determination of micro elements in water should be preceded by preliminary concentration of the test elements.

Concentration of the elements can be effected either by evaporating the water to give a dry residue, or by using such techniques as extraction and coprecipitation with inorganic or organic coprecipitants.

The published methods for the quantitative determination of molybdenum in natural waters [2-5] recommend preliminary concentration of molybdenum followed by photometeric determination.

Spectrographic determination of molybdenum in the dry residues from natural waters has been described previously [6]. This method permits determination of $2 \cdot 10^{-4}$ % of molybdenum in the dry residues with a probable error of ± 10%, and, consequently, for a mineral content of 0.1 g/liter, determination of 0.2 γ of molybdenum in 1 liter of water. The essential drawback of this method is the rapid decrease in sensitivity with increasing mineral content of the water. Thus, the method is no longer fully applicable to water containing 5-10 g/liter of minerals. The way out of the dilemma is preliminary concentration of molybdenum.

Molybdenum can conveniently be concentrated by coprecipitating it with methyl violet tannate [7]. In a medium of 0.2 N hydrochloric acid, where quantitative coprecipitation of molybdenum occurs, such elements as calcium, magensium, sodium, potassium and others which constitute the major part of the mineral component, are not trapped by methyl violet tannate.

Concentration of molybdenum with organic coprecipitants, at the same time, eliminates the interference of the mineral content of the water with its spectrographic determination.

The study of the applicability of the method of concentrating molybdenum with precipitated methyl violet tannate was carried out with the aid of synthetic waters, corresponding approximately in their cation composition to natural waters, and also on natural water free from molybdenum; for this purpose, 200 ml of such water was acidified until the solution was 0.2 N with respect to HCl. Sodium molybdate solution containing 0.3-27 γ of molybdenum was then added; the liquids were finally mixed and precipitation carried out. The molybdenum content of the precipitate was determined spectrographically by evaporating a sample in the carbon electrode of an a.c. arc, with subsequent measurement of the absolute intensity of the most sensitive molybdenum line Mo 1R--3132.6 A, taking into account the near background.

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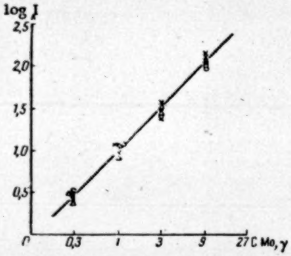

Relation between the intensity of the line Mo - 1 - R = 3132.6 A and the molybdenum content of the sample, after concentration of the molybdenum by coprecipitation with methyl violet tannate from synthetic and natural waters with varying mineral contents:

● – Water with high mineral contents;
o – Water with average mineral contents;
Δ – Water with low mineral contents;
× – Twice-distilled water.

Calibration curves were constructed (Fig. 1) by using standard powders which were photographed on the same photographic plate as the test samples. Standard powders containing 0.3, 1, 3, 9 and 27 γ of molybdenum were prepared by coprecipitating molybdenum from twice-distilled water by the method described.

Results of experiments given in Table 1 and in Fig. 1 show that preliminary concentration of molybdenum by coprecipitation with methyl violet tannate is suitable for water with varying mineral content. The mean probable error of the method is ± 12%.

Results for the determination of the molybdenum content of natural waters are given in Table 2.

The Method Used for Concentrating Molybdenum from Natural Waters

Reagents Required:

1) 2% aqueous solution of methyl violet; 2) 2% aqueous solution of tannin – this should not be kept for more than 2-3 days; 3) hydrochloric acid, about 6 N, distilled in a quartz apparatus; 4) water, twice distilled in an apparatus with a quartz condenser; 5) wash solution: to 1000 ml of water is added 20 ml of hydrochloric acid, 0.5 ml of tannin solution and 2 ml of methyl violet solution; 6) standard molybdenum solution, used for constructing the calibration curve.

a) Stock solution: 15 mg of MoO_3 is dissolved in 15-20 ml of about 0.5 N NaOH, and the solution diluted to 50 ml with water, it is then acidified with 3.5 ml of 6 N HCl and made up to the mark with water; the final solution contains 100 γ/ml of Mo; b) working solution: 1 ml of the stock solution is diluted with water to 100 ml; this solution contains 1 γ/ml of Mo.

TABLE 1

Spectrographic Determination of Molybdenum in Natural and Synthetic Waters with Varying Mineral Contents, after Coprecipitation of Molybdenum with Methyl Violet Tannate. Molybdenum could not be detected in the orginal waters.

Molybdenum, in γ		Error, in %	Molybdenum, in γ		Error, in %	Molybdenum, in γ		Error, in %	Molybdenum, in γ		Error, in %
added	found		added	found		added	found		added	found	
—	0	—	1,0	0,97	—3,0	3,0	2,3	—23	9,0	8,0	—11
0,3	0,25	18	1,0	1,2	+20	3,0	2,8	-6,6	9,0	8,8	—2,2
0,3	0,28	—6,6	1,0	1,2	+20	3,0	2,8	—6,6	9,0	8,9	—1,1
0,3	0,31	+1,6	1,0	1,2	+20	3,0	2,9	—3,3	9,0	9,1	+1,1
0,3	0,33	+10	1,0	0,96	—4,0	3,0	3,0	0	9,0	10,2	+13
0,3	0,36	+18	1,0	1,1	+10	3,0	3,3	+10	9,0	10,6	+18
1,0	0,62	—38	1,0	1,2	+20	3,0	2,8	6,6	9,0	9,0	0
1,0	0,64	—36	3,0	2,3	—23	3,0	3,6	+20	27	30	+11
1,0	0,88	—12				9,0	7,8	+24			

Mean probable error ± 12%.

All the reagents used as well as the ashless filter paper must be checked spectrographically for their molybdenum contents.

Since normal glass may contain molybdenum, coprecipitation should be effected in a quartz vessel.

TABLE 2

Comparative Spectrographic and Photometeric Determination of Molybdenum in Natural Waters

Direct, semi-quantitative spectrographic determination of the dry residues	Quantitative spectrographic determination after concentration of the molybdenum by the recommended method, in γ/l	Photometric determination,* in γ/l	Direct, semi-quantitative spectrographic determination of the dry residues	Quantitative spectrographic determination after concentration of the molybdenum by the recommended method in γ/l	Photometric determination,* in γ/l
Insignificant traces	2.9	1.6	Insignificant traces	2.1	
"	0.8	0.8	"	24.5	0.8
"	0.7	0.8	Traces	6.8	16
Not detected	14.5	14.0	"	12.0	4.8
Insignificant traces	1.85	Traces	Not detected		10.0
Traces	1.3	1.0	Traces	7.8	3.0
			"	10.0	5.0

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* Photometric determination of molybdenum was carried out in the chemical laboratory of the All-Union Scientific Research Institute of Hydrogeology and Engineering Geology (VSEGINGEO) by the method described in [3].

Coprecipitation of Molybdenum. To about 1 liter of natural water filtered if necessary — is added 30 ml of hydrochloric acid followed by 2.5 ml of tannin solution per 100 ml of the water and, dropwise with stirring, 5 ml of methyl violet solution per 100 ml of water. Solution plus precipitate are allowed to stand for 30-40 minutes, after which the precipitate is filtered through a paper filter moistened with wash solution. The first portions of the filtrate are retured for a second filtration. The precipitate is washed 3-4 times with wash solution, and then transferred together with the filter paper to a quartz crucible.

Before ashing, 30, mg of a "base" containing a mixture of equal parts by weight of anhydrous Na_2SO_4, $CaSO_4$, and $MgSO_4$ is placed on the precipitate. This is effected as follows: 1-2 ml of water is added to 30 mg of the mixture mentioned contained in a small beaker; the mixture is brought into suspension and then by means of a capillary, this suspension is poured over all the precipitate. The beaker is rinsed out with 1 ml of water and this also transferred onto the precipitate. The filter paper placed in the crucible is wrapped up by means of a glass rod and moistened with 5-7 drops of sulfuric acid (1 : 1); it is then dried under a drying lamp and ashed in a muffle at a temperature not higher than 500°. The molybdenum is determined in the residue spectrographically.

Spectrographic Determination of Molybdenum in the Concentrates Obtained. Test waters and portions of twice-distilled water to which had been added known amounts of molybdenum were concentrated by the method described. After addition of "base" to all the concentrates, and after ashing, and triturating with alcohol, a residue is obtained from which 15 mg aliquots are weighed out. These portions are placed in the crater of the lower carbon electrodes having an external diameter of 5 mm and inner diameter of 3.5 mm, and a depth of 4 mm. The upper electrode is sharpened to a cone with an area of 1 mm.

Evaporation of the aliquot is carried out in an ac carbon arc arranged vertically; the arc is fed from a 220 volt supply.

A DG-1 arc generator is used. The discharge gap in the firing circuit of the arc is 0.45 mm. The current strength is 16-18 amp. The interelectrode distance is 2 mm. The intermediate diaphragm is equal to 0.5; using this diaphragm it is possible to get normally exposed spectra and to control the distance between the electrodes.

The spectra are photographed in an ISP-22 quartz spectrograph with a three-lens illuminating system, at a slit width for the spectrograph of 0.01 mm.

The plates used are "Spectrographic Type II" with a sensitivity of 32° GOST.

Development is carried out at 18° for a period of 4 minutes in a standard methol- hydroquinone developer.

The blackening of the analytical lines in the molybdenum spectrum is measured on a MF-2 microphotometer.

On the basis of the characteristic curve of the photographic plate, and by means of calculating tables, blackening of the lines in the molybdenum spectrum is converted to line intensity, taking into account the effect of the background.

The sensitivity and accuracy of the method developed for the quantitative determination of molybdenum satisfy the requirements of hydrochemical methods of prospecting for ore deposits.

SUMMARY

1. Precipitated methyl violet, deposited from 0.2 N hydrochloric acid, quantitatively traps molybdenum present in solution; this fact can be used for concentrating the molybdenum with a view to its subsequent spectrographic determination.

2. To each 100 ml of solution, with an acidity of 0.2 N with respect to HCl, is added 5 ml of 2% methyl violet solution and 2.5 ml of 2% tannin solution. The precipitate is filtered, and washed, and, after adding 30 mg of "base," ashed at a temperature not higher than 500°. Molybdenum is determined spectrographically in the residue.

3. It has been shown that by using an a.c. carbon arc as the source of spectrum excitation, and by measuring the absolute intensity of the molybdenum line Mo 1R-3121.6 A, it is possible to determine 0.3-27 γ Mo with a probable error of ± 12%.

4. The technique permits determination of 0.3 γ of molybdenum in 1 liter of water with any mineral content.

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* In Russian.

THE EFFECT OF QUADRIVALENT VANADIUM ON THE REDUCTION OF URANIUM ON A DROPPING MERCURY ELECTRODE

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The polarographic method has been widely used for the determination of small amounts of uranium. The behavior of uranium in all its oxidation states on the dropping mercury electrode has been studied fairly thoroughly; the nature and mechanism of the electrode reactions of uranium have not generated any doubts.

Uranyl salts in weakly acid solutions give two polarographic waves with half-wave potentials at −0.19 volt and −0.92 volt relative to the saturated calomel electrode; the first of them corresponds to the reversible reduction of uranyl ions to quinquevalent uranium ions, while the second corresponds to the two successive stages in the further reduction of quinquevalent uranium to quadrivalent and trivalent uranium [1-4]. Uranium is usually determined polarographically on the basis of the first wave, the height of which, in neutral or weakly acid solutions, is proportional to uranium concentration [1, 5-7]. Nevertheless, the presence of vanadium both quinquevalent and quadrivalent, complicates the polarographic determination of uranium, by increasing the limiting current and leading to the formation of an additional wave at approximately −0.5 volt (with respect to the saturated calomel electrode) which is not present on the polarograms of uranium on its own, or of those of quinquevalent and quadrivalent vanadium. There are references in the literature to the interfering action of vanadium during the polarographic determination of uranium [6], but the reason for this interference is still unknown. Vinogradov [8] has indicated that it should be possible to determine uranium polarographically in the presence of vanadium by using lactic acid as a supporting electrolyte.

The work was carried out on the SGM-8 polarograph made by the "Geologorazvedka" factory; the maximum sensitivity of the galvanometer was $3 \cdot 10^{-9}$ a/mm/m. The constant of the dropping electrode was $m^{2/3}\tau^{1/6} = 2.28\ mg^{2/3}\ sec^{-1}$. Experiments were carried out in an air thermostat fitted with a bimetallic thermoregulator, the temperature being controlled at 20.0 ± 0.2°. The reference electrode was a saturated calomel electrode. All the values of the half-wave potentials quoted in this article are given relative to the saturated calomel electrode.

The solutions were prepared in twice-distilled water. The stock solution of sexivalent uranium was prepared by dissolving uranyl sulfate in water; the uranium content of this solution was established both gravimetrically and titrimetrically. The stock solution of quadrivalent vanadium was prepared by dissolving purified ammonium metavanadate in water and subsequently reducing it with sulfur dioxide. The vanadium concentration was determined titrimetrically. Trivalent vanadium was obtained by reducing the solution of quadrivalent vanadium on a mercury cathode.

The supporting electrolyte was 0.1 N potassium chloride containing 0.55 g-equivalents/liter of hydrochloric acid.

Analysis of Some of the Polarographic Waves of Uranium and Vanadium. In order to study the nature of the polarographic waves of uranium and quadrivalent vanadium, a graphical analysis was made of the waves obtained in 0.1 N KCl and 0.05 N HCl, using the well-known equations for polarographic waves.

$$\varphi = \varphi_{1/2} - \frac{2.3RT}{nF} \lg \frac{i}{i_d - i}.$$

The results of the graphical analysis of the waves of sexivalent uranium in the presence of quadrivalent vanadium, and in the absence of the latter, and also of the waves of trivalent vanadium, are given in Table 1; this table contains the mean values of the half-wave potentials $\varphi_{1/2}$ and the values of 2.3 RT/ nF for the first wave of uranium at −0.2 volt and for the second, additional wave, at −0.5 volt.

TABLE 1

Combination of ions	First wave		Second wave	
	$\varphi_{1/2}$, b	2.3 RT/nF b	$\varphi_{1/2}$, b	2.3 RT/nF b
U^{VI}	−0,197±0,003	0,057±0,002	—	—
$U^{VI}+V^{IV}$	−0,194±0,005	0,056±0,002	−0,507±0,005	0,060±0,002
$U^{VI}+V^{IV}+V^{III}$	−0,199±0,003	0,056±0,001	−0,510±0,003	0,062±0,001
V^{III}	—	—	−0,504±0,004	0,062±0,002

It is evident from the table that the values of the half-wave potentials and the values of 2.3 RT/ nF for the wave of uranyl in the presence of quadrivalent vanadium are the same as in the absence of the latter. This fact indicates that, in the presence of vanadium, the first wave corresponds – in agreement with published results [1-4] – to the reversible reduction of uranyl ions to quinquevalent uranium ions:

$$UO_2^{2+} + e \rightleftarrows UO_2^{+}.$$

The presence of trivalent vanadium in solution has no effect either on the half-wave potential or the height of this wave.

The second, additional, wave corresponds both with respect to position and in form to that of trivalent vanadium, i.e., in accordance with available published results [9, 10], it corresponds to the reversible reduction of trivalent vanadium to the divalent state:

$$V^{3+} + e \rightleftarrows V^{2+}.$$

Polarograms of solutions which contain trivalent vanadium in addition to uranium and quadrivalent vanadium, confirm this. At dropping electrode potentials approximating – 0.5 volt, only one clearly defined wave is observed.

On the basis of these results of graphical analysis, it can be concluded that since the uranium wave in the presence of quadrivalent vanadium corresponds to the reduction of sexivalent uranium to the quinquevalent state, the increase in its height is connected with the formation of additional amounts of UO_2^{2+} ions on the electrode surface; these UO_2^{2+} ions, together with trivalent vanadium ions, are formed in the neighborhood of the electrode as a result of chemical oxidation of quinquevalent uranium by quadrivalent vanadium, probably according to the reaction:

$$UO_2^{+} + VO^{+2} + 2H^{+} \rightleftarrows UO_2^{2+} + V^{3+} + H_2O.$$

The Oxidation-Reduction Reaction between Quinquevalent Uranium and Quadrivalent Vanadium. The possibility that such a reaction occurs is confirmed by results on oxidation-reduction potentials. The formal potential of the system U^{VI}/U^{V} in 0.1 N KCl and 0.1 N HCl is + 0.062 volt [11], while the value of the normal oxidation-reduction potential of the system V^{IV}/V^{III} is + 0.314 volt on the hydrogen scale [12].

In order to confirm the possiblity of an oxidation-reduction reaction between quinquevalent uranium and quadrivalent vanadium, quinquevalent uranium was titrated amperometrically with a solution of quadrivalent vanadium sulfate.

Quinquevalent uranium was prepared together with sexivalent uranium by reducing uranyl sulfate with hydroge in the presence of smooth platinum; its concentration was determined from the height of the anodic part of the U^{VI}/U^{V} wave. Titration was carried out in 0.1 N KCl and 0.005 N HCl; at this concentration of hydrogen ions in solution, quinquevalent uranium is most stable. As $VOSO_4$ solution was added, the height of the anodic part of the uranium wave decreased, while that of the cathodic part increased correspondingly: the total height of the anode-cathode wave remained constant throughout.

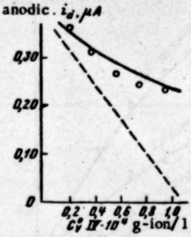

Fig. 1. Amperometric titration of quinquevalent uranium with $VOSO_4$.

In Fig. 1. is shown the results of such a titration carried out with a solution containing $1.07 \cdot 10^{-4}$ g-ion/ / liter of UO_2^+ and $0.91 \cdot 10^{-4}$ g-ion/ liter of UO_2^{2+}, and using a $0.5 \cdot 10^{-3}$ M solution of $VOSO_4$; the circles represent the values obtained experimentally for the anodic diffusion current, corrected for change in volume on addition of $VOSO_4$ solution. As Fig. 1 shows, these points lie on a curve, which, with increasing vanadium concentration, acquires a constantly decreasing slope. That the curve has this shape can be explained on the grounds that the reaction considered does not go to completion; the equilibrium state is already reached at considerable values of the concentration of UO_2^+ in solution. The dotted line is the theoretical curve for amperometric titration in the case where the reaction proceeds almost to the end, i.e., in the case where the diffusion current would be equal to zero, on addition of the equivalent amount of quadrivalent vanadium.

For the reaction

$$UO_2^+ + VO^{2+} + 2H^+ \rightleftarrows UO_2^{2+} + V^{3+} + H_2O$$

the numerical value of the equilibrium constant calculated from the values of the normal oxidation-reduction potentials (for $[H^+] = 5 \cdot 10^{-3}$), is equal to:

$$K = \frac{[UO_2^{2+}]\,[V^{3+}]}{[UO_2^+]\,[VO^{2+}]} = 1{,}6\,.$$

The expression for the equilibrium constant allows us to calculate the equilibrium concentration of UO_2^+ for any concentration of VO^{2+} added to the solution. When the initial concentrations of sexi- and quinquevalent uranium before starting a titration are $C^0_U VI$ and $C^0_U V$, while the concentration of quadrivalent vanadium added is $C^0_U IV$, and X g-ion/ liter of V^{IV} reacts, then, in accordance with the equation for the reaction, the equilibrium concentrations will be expressed as follows:

$$C_U{}^{VI} = C^0_U{}^{VI} + X, \quad C_V{}^{III} = X,$$
$$C_U{}^{V} = C^0_U{}^{V} - X, \quad C_V{}^{IV} = C^0_V{}^{IV} - X.$$

Then, for the equilibrium constants, we can write:

$$K = \frac{(C^0_U{}^{VI} + X)\cdot X}{(C^0_U{}^{VI} - X)\,(C^0_{VI}{}^{V} - X)} = 1{,}6.$$

Solving this quadratic equation with respect to X, we get the values of the equilibrium concentrations of quinquevalent uranium $C_U V = C^0_U V - X$ and, consequently, the values of the anodic diffusion current for all values of $C^0_{V} IV$ for the given original concentrations $C^0_U VI$ and $C^0_U V$.

The continuous line in Fig. 1 represents the theoretical curve calculated in this way, for the amperometric titration of quinquevalent uranium with a solution of quadrivalent vanadium. As can be seen from Fig. 1, the experimental points lie quite satisfactorily on the theoretical amperometric titration curve, constructed by taking into account the theoretically calculated equilibrium constants of the reaction; this seems to be confirmation of the possibility of the occurrence of an oxidation-reduction reaction between quinquevalent uranium and quadrivalent vanadium, as a result of which ions of sexivalent uranium and trivalent vanadium are formed.

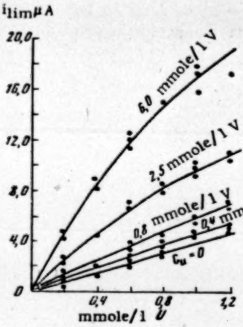

Fig. 2. Relation between the limiting current and uranium concentration.

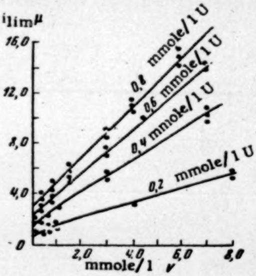

Fig. 3. Relation between the limiting current and vanadium concentration.

In the case of the reduction of sexivalent uranium in the presence of quadrivalent vanadium on a dropping electrode, all the sexivalent uranium formed as a result of chemical reaction on the electrode is reduced again on the electrode, thereby continuously supplying quinquevalent uranium ions for chemical reaction, and removing sexivalent uranium ions from the sphere of reaction; under such conditions, the rate of chemical reaction becomes high enough to effect an increase in the limiting current of uranium, which is several times greater than the diffusion current.

The phenomenon of an increase in the polarographic limiting current as the result of the occurence of a chemical reaction at the electrode surface is not a new one. Similar phenomena have been observed during the reduction on a dropping electrode, of trivalent iron ions in the presence of hydrogen peroxide [13], of sexivalent tungsten in the presence of perchloric acid [14], of quadrivalent titanium in the presence of hydroxylamine [15], and of the oxalate complex of titanium in the presence of ClO_4^- ions [16].

The Relation Between the Limiting Current and Uranium and Vanadium Concentrations. The relation between the limiting current and uranium concentration was studied over a concentration range up to 1.2 millimoles/liter for four values of the vanadium concentration in solution. The results are given in Fig. 2, where each curve corresponds to a definite constant concentration of vanadium.

The relation between the limiting current and vanadium concentration is shown in Fig. 1. Each curve represents the change in the limiting current as a function of vanadium concentration in the solution for a given uranium concentration. By studying the relation between the slope of the linear parts and the uranium concentration, an empirical equation was obtained which expresses the relation between the limiting current and the concentration of uranium and vanadium respectively:

$$i_{lim.current} = C_V (2.14 + \ln C_U) + K(C_U + 0.05),$$

where $i_{lim.current}$ is the limiting current, C_U is the uranium concentration, and C_V is the vanadium concentration; and K is the Ilkovich constant which is equal to $605\, nD_n^{1/2} \cdot m^{2/3} \cdot \tau^{1/6}$

The values of the limiting current calculated by means of this equation coincide satisfactorily with the values obtained experimentally over the uranium concentration range 0.2 to 1.2 millimoles/liter, and the vanadium concentration 1 to 8 millimoles/liter (at a temperature of 20° and a hydrochloric acid concentration of 0.05 N).

A study of the relation between the limiting current of the second, additional wave at −0.5 volt and the concentration of uranium and vanadium in solution, showed that the nature of this relation is identical to that for differences between the limiting current of uranium in the presence of vanadium $i_{\text{lim.current}}$ and its diffusion current in the absence of the latter i_d. The difference $i_{\text{lim.current}} - i_d$ is a part of the total general current determined by the occurrence of a chemical reaction at the electrode surface. According to the equation given above for this reaction, sexivalent uranium and trivalent vanadium are formed in the layers near the electrode in equivalent amounts; therefore the difference $i_{\text{lim.current}} - i_d$ and the value of the limiting current of the second wave i', corresponding to the reduction of trivalent vanadium, can only differ from each other by a constant multiplier equal to the square root of the ratio of the diffusion coefficients of the UO_2^{2+} and V^{3+} ions. In Table 2 are given the values of the ratio $i'/i_{\text{lim.current}} - i_d$ for several different concentrations of uranium and vanadium in solution.

TABLE 2

c_U mmole/1	c_V mmole/1	$i_{\text{lim}} - i_d$ (μamp)	i', μamp.	$i'\mu$ $-i_d$
0,2	0,4	0,25	0,30	1,2
0,2	0,8	4,94	6,34	1,3
0,4	0,4	0,48	0,60	1,2
0,4	7,0	8,74	12,32	1,4
0,6	0,8	1,37	1,70	1,2
0,6	3,0	5,19	6,60	1,3
0,8	3,0	5,88	6,85	1,2

The values for $i'/i_{\text{lim.current}} - i_d$ can be regarded as constant (the mean value is equal to 1.2); the deviations observed are the result of errors in measuring the wave height.

Effect of the Acidity of the Solution on the Limiting Current. It is known from published results [17-19] that the disproportionation of quinquevalent uranium ions into hexa- and quadrivalent ions at the surface of the dropping electrode starts to affect the value of the limiting current appreciably at a hydrogen ion concentration in excess of 0.2 g-ion/liter. With increasing acidity of the solution, the disproportionation rate increases; a consequence of this is a continuous increase in the limiting current of uranium up to the point where the quinquevalent uranium formed on the electrode surface does not disproportionate completely, as a result of which the limiting current becomes a constant and is double the diffusion current of uranium in weakly acid solutions.

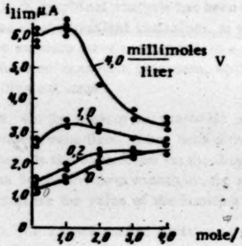

Fig. 4. Relation between limiting current and hydrochloric acid concentration.

When quadrivalent vanadium is present in a strongly acid solution, oxidation of quinquevalent uranium in the layers near the electrode by the ions of quadrivalent vanadium is superimposed on the disproportionation of quinquevalent uranium. In Fig. 4. is shown the relation obtained experimentally between the limiting current of uranium (0.4 millimoles/liter), both in the absence of vanadium, and in its presence (for three different vanadium concentrations), and the hydrochloric acid concentration of the solution. As this Fig. shows, the limiting current increases in all cases with increasing acid concentration up to an acid concentration of 1 N; the maximum value is reached at this point, thereafter there is a sharp drop with further increases in the acid concentration, and the value tends to the value for the limiting current in the absence of vanadium.

In all probability, with increasing acidity of the solution, the rate of oxidation of quinquevalent uranium increases; but, at acid concentrations in excess of 1 N, the rate of disproportionation of the quinquevalent uranium increases to a considerably greater extent, thanks to which there is also observed a drop in the value of the limiting current at high acid concentrations. This fact serves as indirect confirmation of the occurrence of a chemical oxidation of quinquevalent uranium by quadrivalent vanadium in the layers near the electrode.

Effect of Temperature on the Limiting Current. The effect of temperature on the value of the limiting current for the reduction of uranium in the presence of vanadium, also indicates the occurrence of a chemical reaction on the electrode surface. At ordinary temperatures the rate of most chemical reactions increases by 2-3 times on increasing the temperature by 10°, while for diffusion processes the value of the temperature coefficient amounts to only 1.15-1.20. Thus measurements of the value of the temperature coefficient of the limiting current $i_{\text{lim.current } t+10} / i_{\text{lim.current } t}$ may indicate the occurrence of a chemical reaction in the layers near the electrode, the rate of which may partially or completely determine the value of the limiting polarographic current.

TABLE 3

C_V, μmoles/ / liter, t°	Temperature, in °C				
	0-10	10-20	20-30	30-40	40-50
0	1.18	1.15	1.13	1.12	1.10
0.2	1.33	1.25	1.20	1.17	1.14
1.0	1.58	1.36	1.27	1.22	1.18
6.0	2.06	1.53	1.35	1.26	1.20

A study of the relation between the limiting current and temperature was carried out in the temperature range 5-50°. The values of the temperature coefficients of the limiting current of uranium (0.4 millimole/liter) $i_{\text{lim.current } t+10} / i_{\text{lim.current } t}$ calculated from the experimental results, in relation to the temperature and vanadium concentration in solution, are given in Table 3.

The values for the temperature coefficients given in this Table indicate qualitatively that the limiting current for the reduction of uranium in the presence of vanadium, together with the diffusion process, is also determined by the rate of the chemical oxidation of quinquevalent uranium by quadrivalent vanadium which occurs on the surface of the droppping electrode.

We have learned that V. G. Sochevanov and N. V. Shmakov, as a result of work carried out by them in 1953, came to a similar conclusion regarding the mechanism of the effect of vanadium on the reduction of uranium on a dropping mercury electrode.

SUMMARY

1. A graphical analysis has been made of the polarographic wave obtained for sexivalent uranium in the presence of quadrivalent vanadium, as well as an analysis of a second, additional wave; as a result it has been found that the uranium wave corresponds to a reversible reduction of uranyl ions to quinquevalent uranium ions as in the case where no vanadium is present, while the additional wave corresponds to the reduction of trivalent vanadium to the divalent state.

2. On the basis of this graphical analysis of the polarographic waves of solutions containing uranium and quadrivalent vanadium, it has been shown that the reason for the increase in the uranium wave in the presence of vanadium is the occurrence on the dropping electrode surface of a chemical oxidation reaction of quinquevalent uranium by quadrivalent vanadium, the rate of this reaction, together with the diffusion process, are the determining factors for the value of the limiting current.

3. An amperometric titration of quinquevalent uranium with quadrivalent vanadium sulfate has demonstrated the possibility of such an oxidation-reduction reaction.

4. Results obtained during a study of the effect of the acidity and temperature of the solution on the limiting current confirm the occurrence of a chemical reaction in the layers near the electrode.

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AN ANALYTICAL STUDY OF THE PRECIPITATION OF QUADRIVALENT URANIUM BY SODIUM HEXAMETAPHOSPHATE

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Methods are known for the precipitation of uranium by means of the salts of ortho-, and pyrophosphoric acids and by hypophosphates [1-3]. An essential drawback of the gravimetric method based on precipitation of uranyl orthophosphate followed by calcination to the pyrophosphate, is the variable composition of the compounds formed. Precipitation with orthophosphate has only been used for separating uranium from certain elements, mainly from vanadium [4]. Uranium is quantitatively precipitated as its orthophosphate in weakly acid or weakly alkaline media. Consequently, the phosphate method can be used for separating uranium from a very limited number of elements. The specificity of the method can be increased in two ways: a) by establishing more specific conditions for the precipitation of sexivalent uranium, e.g., by addition of Complexon III [5]; b) by precipitating uranium in a mineral acid medium in a quadrivalent state. At present two variants of the method have been developed for ore analysis; they differ from each other in the method used for reducing U^{VI} to U^{IV} [6].

Collectors – thorium and zirconium phosphates – are used for isolating small amounts of uranium. It is possible that the sparingly soluble compound formed between hexametaphosphates and quadrivalent uranium may be of interest for separating small amounts of uranium.

Sodium hexametaphosphate has been used hitherto as a complexing agent [7-8].

Solutions of uranyl acetate were prepared for the work; they were standardized vanadometrically [9]. Uranium was reduced in a special semi-micro electrolytic cell using a current of 2 amps and 5 volts in the course of 30 minutes.

Sodium hexametaphosphate was obtained by heating sodium dihydrogen phosphate $NaH_2PO_4 \cdot 2H_2O$ in a platinum basin for 10-15 minutes at 620° and then rapidly cooling the melt formed. 2% aqueous solutions were prepared from the ground melt. Solutions of higher concentration could not be prepared in the cold.

The aqueous hexametaphosphate solutions show a neutral reaction and are fairly stable in the cold; nevertheless, on heating or on acidification, they hydrolyze [7, 10]. The sodium hexametaphosphate content of the solution which was shown to be 96.04% was established by titration with barium chloride [7]. Acidimetric titration and appropriate qualitative reactions showed that in a freshly prepared solution, pyro- and orthophosphates are almost absent; nevertheless they are gradually formed when the solution is allowed to stand.

Experiments showed that on addition of hexametaphosphate to an acid solution of quadrivalent uranium in the cold, no visible changes were evident. When, however, the solution was heated to 60-80°, a precipitate with a greenish color separated out. On increasing the temperature further, the volume of the precitate decreased appreciable, as was to be expected, while continued boiling led to the complete solution of the precipitate. It was also noticed that on addition of large amounts of sodium hexametaphosphate (e.g., 0.5 g) to 10-25 ml of solution containing 25 mg U, the latter was not precipitated either in the cold or on heating.

In order to establish the conditions necessary for the quantitative precipitation of uranium, a solution containing quadrivalent uranium, and sulfuric acid or perchloric acid, was heated on a water bath to a certain temperature, and a freshly prepared 2% solution of sodium hexametaphosphate added slowly, dropwise. The precipitate formed was kept on the water bath for a certain time, and then centrifuged; it was finally dissolved on heating in concentrated sulfuric acid. The amount of uranium was determined vanadometrically.

A series of experiments showed that uranium is precipitated to the greatest extent by heating the solutions to 60-70° before precipitation (Table 1); after precipitation, it is necessary to heat the solution for 10-15 minutes on a water bath (Table 2).

TABLE 1

Effect of the Temperature of the Solution on the Precipitation of Uranium (24.04 mg of U taken)

Temperature, in °C	Volume of 0.02 N NH_4VO_3, in ml	U found	
		in mg	in %
18-20	–	Precipitate not formed	
60-70	9.35	22.25	92.76
100	8.10	19.28	80.20

TABLE 2

Effect of Duration for which Solution plus Precipitate are Heated on Completness of Precipitation of Uranium (24.04 mg U taken)

Time of heating, in minutes	Volume of 0.02 N NH_4VO_3, in ml	U found	
		in mg	in %
15	9.35	22.25	92.76
50	1.15	2.74	11.39
150	–	Precipitate dissolves completely	

In perchloric acid solutions, quadrivalent uranium is quantitatively precipitated over a narrow hydrogen ion concentration corresponding to 3 N (Fig. 1, Curve 2). The comparatively sharp decrease in the amount of uranium precipitated, with an increase or decrease in acidity on each side of this optimum acidity, is obviously connected, in the first instance, with the enhanced solubility of the compound formed as a result of the hydrolysis of the hexametaphosphate, and in the second case with the possibility of the formation of a complex compound of uranium.

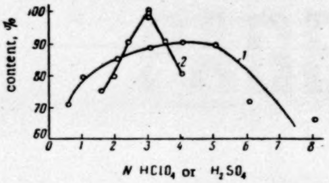

Fig. 1. Effect of acidity on precipitation of uranium with sodium hexametaphosphate.
1) Precipitation in H_2SO_4 media; 2) in $HClO_4$ media.

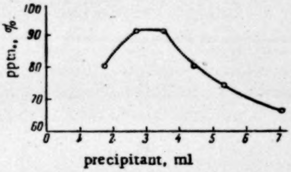

Fig. 2. Effect of the amount of hexametaphosphate on the precipitation of uranium in a medium of H_2SO_4.

Quadrivalent uranium is not completely precipitated in sulfuric acid solutions (Fig. 1, Curve 1); this fact has also been established by other research workers for the orthophosphate of quadrivalent uranium [6, 11], and is explained, presumably, by the formation of complex uranium compounds with the sulfate. Incomplete precipitation in sulfuric acid solutions was observed during a study of the effect of various amounts of sodium hexametaphosphate. It is clear from Fig. 2 that maximum precipitation of uranium occurs on adding 2.6-3.5 ml of a 2% solution of the precipitant when the total volume is 20 ml; this corresponds to a molar ratio of U : PO_3 = 1 : 6 - - 1 : 8.

In perchloric acid solutions, completeness of precipitation of uranium depends not so much on the molar ratio of uranium to hexametaphosphate as on the concentration of the latter in solution. Almost complete precipitation of more than 2 mg of uranium in 3 N perchloric acid is achieved at a final concentration of hexametaphosphate in solution of 0.30-0.35% (Table 3). Nevertheless, under the conditions indicated, a precipitate is not formed for uranium contents of about 0.2 mg in 20 ml of solution.

Thorium was used as a coprecipitant for isolating small amounts of uranium. It was established that addition of 5 ml of 0.5% thorium chloride solution ensures complete precipitation of traces of uranium. Increasing the amount of coprecipitant does not lead to an increase in the amount of uranium precipitated, while at the same time it complicates further operations because of the large volume of precipitate. Uranium can be precipitated in the presence of thorium not only on heating, but also in the cold. For example, for contents of 2-3 mg uranium in solution, 99-100% of this element is precipitated, while for contents of 0.1-0.3 mg, the amount precipitated is about 70-80%. In the latter instance, in order to achieve complete precipitation, it is necessary to heat the solution to 60-70°. The possibility of precipitating small amounts of uranium together with thorium from a medium of 3 N $HClO_4$, has advantages over precipitation from 0.25-0.35 N HCl as the orthophosphate [6].

TABLE 3

Precipitation of Uranium by Hexametaphosphate in Perchloric Acid Solutions [$(NaPO_3)_6$ concentration 0.30-0.35%]

U taken, in mg	NH_4VO_3 used up, in ml	U found*	
		In mg	In %
24.04	10.05 (0.02 N)	23.01	99.46
2.53	10.68 (0.002 N)	2.54	100.40
2.53	10.60 (0.001 N)	2.52	99.60

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* Mean of 3-4 determinations

The addition of hexametaphosphate in amounts greater than the molar ratio Th : PO_3^- = 1 : 5, leads to low results for uranium. Accordingly, the maximum amount of reagent corresponds to a 25% excess of it with respect to thorium, if it is assumed that $Th(PO_3)_4$ is formed.

TABLE 4

Behavior of the Precipitate Towards Various Wash Liquors

Wash liquor	Color observed	Mean value of D	U found, in g
Cold water	−	−	−
Hot water	+	0.027	0.0040
Water + C_2H_5OH in the proportion 1 : 1	−	−	−
Water + C_2H_5OH in the proportion 1 : 2	+	0.015	0.0021
Water + C_2H_5OH in the proportion 1 : 3	+	0.010	0.0015
$(NaPO_3)_6$ solution, 0.0025 g/ ml	+	0.023	0.0020
$HClO_4$ solution (20 ml of acid in 1 liter of water)	−	−	−

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* +) the solution is colored yellow
−) colorless solution.

In order to choose a suitable wash liquor, the precipitate of uranium obtained under the optimum precipitation conditions was shaken up with various wash liquors for 30 minutes at 20°. The precipitate was then centrifuged, and the uranium content of 5 ml of centrifugate determined photometrically by the peroxide method. Only the optical density of solutions which had a weak-yellow color was measured (Table 4).

When the precipitate was washed with cold water and with a mixture of water and alcohol, the precipitate was found to be peptized. When hot water or a dilute solution of sodium hexametaphosphate was used, appreciable amounts of the precipitate dissolved. The best wash liquor proved to be a dilute solution of perchloric acid (e.g., 0.01 N).

The method used for determining uranium may be stated concisely as follows:

20 ml of 3 N perchloric acid containing quadrivalent uranium* is heated to 60-70°. When not less than 2 mg of uranium is present, 3.5 ml of a freshly prepared 2% solution of sodium hexametaphosphate is added. In order to precipitate small amounts of uranium (tenths of a milligram), 5 ml of a 0.5% solution of thorium chloride solution is added, followed by precipitant solution in an amount which is 25% in excess with respect to the thorium. For improved coagulation of the precipitate, the solution is heated on a water bath for 10-15 minutes. The precipitate is centrifuged and then washed with 0.01 N perchloric acid; it is finally dissolved in 10-12 ml of concentrated sulfuric acid on heating. Uranium determination is finished vanadometrically.

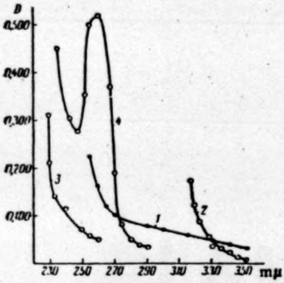

Fig. 3. Absorption curves for uranium solutions. 1) Perchloric acid solution of U^{VI}; 2) perchloric acid solution of U^{VI}; 3 and 4) perchloric acid solution of U^{IV}; in the presence of sodium hexametaphosphate.

TABLE 5

Precipitation of Uranium with Sodium Hexametaphosphate

U taken, in mg	U found, in mg	Error	
		in mg	in %
28,15	27,97	—0,18	—0,64
28,38	28,56	0,18	+0,63
28,38	28,44	+0,06	+0,21
28,38	28,08	—0,30	—1,06
2,02	2,02	0	0
2,02	1,98	—0,04	—1,98
2,02	2,05	+0,03	+1,49
0,250	0,249	—0,001	—0,40
0,250	0,252	+0,002	+0,80
0,190	0,190	0	0
0,190	0,191	0,001	+0,53
0,190	0,190	0	0

Under the conditions given above for the determination of uranium, tri- and quadrivalent vanadium (2-20 mg), iron, copper (up to 200 mg of each), and other di- and trivalent elements are not precipitated.

As noted above, under certain conditions, formation of complex compounds of uranium with hexametaphosphate is presumably possible. We have confirmed this possibility by carrying out a spectrophotometric study of the solutions. Using an SF-4 spectrophotometer, absorption curves were taken for quadri- and sexivalent uranium in the absence and in the presence of sodium hexametaphosphate, in amounts at which the uranium is not precipitated; namely, at ratios of $U : PO_3^- = 1 : 48$ for U^{IV} and $1 : 16$ for U^{VI}. The optical density of sodium hexametaphosphate solutions is zero in the region 225-290 mμ. The null solutions were 3 N perchloric acid solutions of sodium hexametaphosphate of the appropriate concentration.

On the basis of the results obtained, (Fig. 3), it can be concluded that U^{VI} and U^{IV} form complex compounds with hexametaphosphate. In the case of U^{VI}, on addition of hexametaphosphate, there is an increase in the optical density at the corresponding wave-lengths (Curves 1 and 2); while in the case of U^{IV} there is a change in the nature of the curve, with the appearance of a maximum on the absorption curve at 260 mμ (Curves 3 and 4).

SUMMARY

The possibility of precipitating quadrivalent uranium with sodium hexametaphosphate has been established. The effect of various factors on the completeness of precipitation of uranium has been studied. It has been found that complete precipitation can be effected from 3 N perchloric acid. Thorium has been used as a coprecipitant for the complete separation of small amounts of uranium.

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*Obtained by electrolysis on a mercury cathode.

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*Original Russian pagination. See C. B. Translation.

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DETERMINATION OF TRACES OF COPPER IN AGRICULTURAL MATERIALS BY MEANS OF PAPER CHROMATOGRAPHY

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The chromatographic method has still not found sufficiently wide application in the analysis of agricultural chemicals. Several papers have been devoted to chromatographic studies of organic insecto-fungicides [1-6]. Due attention has not been given to the application of chromatography in the analysis of mineral preparations. At the same time, despite the large number of macro methods available [7], satisfactory methods have not yet been developed for determination of small amounts of "insecto-fungicide" ions (Cu^{2+}, Hg^{2+}, Ba^{2+}, Zn^{+2}, AsO_3^{3-}, AsO_4^{3-}, F^-, SiF_6^{2-}, CN^-) in agricultural materials (grain, fruit, leaves, etc.). Paperchromatography may be able to play an important part in solving this problem.

We have studied the possibility of using paper chromatography for the quantitative determination of traces of copper. We decided on using Cu^{2+} cations because copper-containing preparations (copper sulfate, preparation AB, Paris Green, copper oxychloride, Bordeaux Mixture, copper trichlorophenolate, copper naphthenate) are widely used in agriculture.

Of the methods published in the literature, for carrying out quantitative determination of materials located on paper [8, 9], of interest in the present endeavor were the following approximate, but simple and relatively rapid methods: a) direct comparison of the zones developed with chromatographic standards; b) methods based on the existence of a relation between the concentration of the test component and the area of its zone on the chromatogram:

$$S = a \operatorname{Log} c + b$$

where S is the area of the spot of the test component on the chromatogram; c is the concentration of the component in the original solution; a and b are empirical constants.

The latter method was suggested [10] for the quantitative study of amino acids. Its suitability for determining mineral ions by means of circular chromatograms has not been studied. Accordingly, it was necessary: 1) to examine the relation between the concentration of Cu^{2+} ions and the width of its localization zone on the developed circular chromatograms; to check on the reproducibility of the R_f values under the experimental conditions adopted. After this it should be possible to develop a technique for determining traces of copper in plant material.

Determination of R_f Values, and the Width of the Cu^{2+} Zones on Paper. Preliminary tests showed the correctness of Ivanova's conclusion that for the chromatographic separation of inorganic ions, the best filter paper is "blue band" paper. Accordingly, in the course of the work described here, circular ashless "blue band" filter papers TU MMP RSFSR No. 304-53 with a diameter of 12.5 cm were used exclusively. Solutions were prepared from chemically pure reagents and twice-distilled water.

In all cases, 0.05 ml of solutions containing various amounts of Cu^{2+} ions were placed on the center of the paper by means of a micropipet. The original spot thus formed was ringed with pencil, i.e., its position on the paper was fixed. After the paper had been dried, a "tongue" 40 mm long and 4 mm wide was cut in the paper.

The chromatographic cells used were desiccators in each of which was placed a crystallizing basin to serve as support for the filter paper. Tall crucibles containing the solvent were placed in the middle of the crystallizing basin.

The solvent used for developing the chromatograms was both simple and readily available: 90% by volume of 80% ethanol and 10% of 5 N hydrochloric acid. A chromatogram took 4 hours to run. The developer used for the Cu^{2+} ions was a 10% solution of $K_4[Fe(CN)_6]$.

For determining R(f) values, we took the boundary of the spot formed as the beginning of the path of the Cu^{2+} ions, while the outer boundary of the circular zone formed after development was taken as the end of the path. The path taken by the solvent front was taken from the center of the chromatogram, i.e., from the center of the filter. In this way about 200 chromatograms were taken; each value given below represents the mean of 3-4 determinations.

The technique adopted permitted the determination of 5 γ of Cu^{2+}, i.e., it possessed an accuracy sufficient for practical purposes.

Table 1 contains the R_f values, and the width of the circular zones of the Cu^{2+} ions for the concentration range 5-50 γ.

TABLE 1

Determination of R_f Values and the Width of the Cu^{2+} Zones

Amount of Cu^{2+} in γ placed on the filter	R_f value	Zone width, in mm
5	0.28	1.0
10	0.29	1.5
20	0.29	2.0
30	0.30	3.0
40	0.29	4.0
50	0.28	4.5

It is evident from Table 1 that under the experimenta conditions used, the R_f value for Cu^{2+} ions is a constant. The deviations from the mean values given did not exceed ± 0.02-0.03.

For quantities of copper in the range 5-50 γ there was found to be linear relation between the concentration of the test ion and the width of its circular zone on the chromatogram. In each case it proved possible to construct a calibration curve for the approximate determination of Cu^{2+}. Thus, by working with circular chromatograms there is no need to calculate the area of the spot for the component located on paper. All the same, this quantitative method is only possible for relatively low concentrations of the test ion. We established that on placing appreciable (more than 100 γ) amount of Cu^{2+} ions on the paper, the relation is no longer linear. Thus, in the range 100 to 200 γ of Cu^{2+} ions, the zone width only increases from 5 to 7 mm, i.e., by only 2 mm. Consequently, for quantities of the order to 100 γ and more of copper, determination of the latter on the basis of the zone widths of circular chromatograms is difficult.

TABLE 2

Chromatographic Determination in Agricultural Materials

Cu^{2+} taken, in γ	Cu^{2+} found, in γ
5	5
9	10
12	15
15	15
23	25

TABLE 3

Concentration of Solutions for Preparation of Chromatograms

No.	$CuSO_4 \cdot 5H_2O$ concentration, in g/liter	Amount of Cu^{2+} ions in 0.05 ml of the solution prepared, in γ
1	0.393	5
2	0.786	10
3	1.572	20
4	2.358	30
5	3.144	40
6	3.930	50

Description of the Method. The relationship found was used for the quantitative determination of traces of copper in agricultural materials (grain, fruit, leaves). First, known amounts of some copper-containing preparation (AB, cupric sulfate, Paris Green, etc.) were placed on some plant material. When this was done the copper dosage used was known to be less than that adopted in actual practice. For example, the amount of preparation AB actually placed on the plant material was equivalent to 1 kilogram per ton of wheat grain, although in agricultural practice larger amounts are used — up to 2.5 kilogram per ton. In this way we took into account natural losses of copper.

The amount of Cu^{2+} ions was then determined on the various plant materials by the chromatographic method described. The results obtained (Table 2) show that this approximate method is applicable for practical purposes.

Analytical Procedure. Before carrying out an analysis, it is essential to prepare chromatographic standards and construct a calibration curve on their basis. For this purpose, a series of chromatograms with successively increasing amounts of copper ions 10, 20, 30, 40, and 50 γ are taken. The concentrations of the copper solutions are shown in Table 3.

Six "blue band" filter papers 12.5 cm in diameter are taken and 0.05 ml of one of the copper solutions indicated above placed on the center of the paper. The solution is not poured onto the paper, but allowed to leak out by capillary action.

The filters are dried and the "tongues" cut out of them, 4 mm wide and 40 mm long. The "tongue" should be marked out on the filter paper with a pencil before placing the solution of copper ions on it. The desiccators used as chromatographic tanks are opened, and the "tongues" of the filter papers placed in crucibles containing solvent (10 ml), the crucibles being placed in the middle of crystallizing basins contained in the desiccators. The lids of the desiccators are replaced and the chromatograms allowed to run.

The developer used is a mixture containing 90% by volume of ethanol and 10% 5 N hydrochloric acid. Developing of the primary chromatogram with this solvent takes 4 hours. The filter papers are then removed from the desiccators, the solvent allowed to evaporate, and the papers developed by spraying them with 10% $K_4[Fe(CN)_6]$ solution from a glass sprayer (metallic ones are not suitable).

When the filter papers have been dried, the widths of the brown-red rings of Cu^{2+} are measured on each paper, and a calibration curve constructed on the basis of the results obtained. It is useful to keep the standard chromatograms, since during determination of very small amounts of copper (5-10 γ) the intensity of the color of the circular zones is of some significance.

When preparing the calibration curve, and also in carrying out an actual analysis, it is essential to observe strictly the conditions used for preparing the chromotograms. All operations should be carried out in exactly the same way. Desiccators, crystallizing basins, beakers, and filters should all be of the same size. The same micropipet should be used in all cases.

In order to get comparable results, strict observance of the dimensions of the "tongues" is of essential importance; the distance between the surface of the filter paper and the level of the solvent in the crucible is of equal importance. When the standard chromatograms have been obtained and a calibration curve constructed, analysis of the test samples is carried out.

All copper-containing agricultural materials (cupric sulfate, preparation AB, Paris Green, Bordeaux Mixture, copper oxychloride) readily dissolve in hydrochloric acid. Accordingly, 1-5 g of test material, treated beforehand with a copper-containing material – e.g. grain dusted with preparation AB – is washed with 2 N HCl, taking as a basis 1 ml of acid per gram of test material. The solution obtained is filtered through ashless "blue band" paper free from copper. 0.05 ml of this solution is then placed on the center of a filter. The chromatogram is allowed to run, and developed, etc., exactly as in the case of preparation of standards. The width of the zone is then measured, and, using the calibration curve, the approximate copper content determined.

The method described is only suitable for determining copper on the surface of plant material.

It is very useful to be able to identify the copper-containing preparations on the basis of chromatographic standards prepared once and for all and stored in the laboratory. For this purpose 100 mg aliquots of test material (AB, Paris Green, etc.) are dissolved in 5 ml of 2 N HCl, the solutions filtered and chromatographic standards obtained for each preparation as described above.

By choosing the appropriate solvent and developer, it should be possible to use paper chromatography for the determination of residual amounts of other ions (Hg^{2+}, Ba^{2+}, Zn^{2+}, AsO_3^{3-}, AsO_4^{3-}, F^-, SiF_3^{2-}, CN^-) on agricultural materials.

SUMMARY

1. R_f values have been determined for Cu^{2+} ions during chromatographic separation on "blue band" paper, using the following solvent: 90% (by volume) of 80% ethanol and 10% of 5 N hydrochloric acid (by volume).

2. It has been shown that within the limits of 5 to 50 γ of Cu^{2+}, there is a reasonably linear relation between concentration of copper ions and the width of the circular zones obtained on the chromatograms.

3. A new method has been developed for the determination of small amounts of copper in agricultural materials by means of paper chromatography.

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FORMATION OF SULFONIUM SALTS AS A METHOD FOR THE DETERMINATION OF ORGANIC SULFIDES

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For the quantitative determination of organic sulfides a number of authors [1-3] have used the capacity of the sulfides to react with bromine or iodine. In other methods [4-6] solutions of potassium iodate or of potassium bromide-bromate have been used for titrating the sulfides. The reaction of sulfides with heavy metal salts has also been employed by many authors [7-10]. The most suitable reagent for the quantitative extraction of sulfides is mercurous nitrate. The presence of unsaturated or aromatic compounds makes quantitative determination of sulfides impossible. At the same time, the determination of sulfides in petroleum products and in other complex mixtures is of considerable interest from the point of view of controlling technological processes and for developing methods of desulfurizing oils and motor fuels.

Organic sulfides are capable of forming sulfonium compounds according to the following scheme:

$$R_1 - S - R_2 + R_3 - Hal \rightarrow [R_1 R_2 R_3 S]^+ Hal^-$$

The compounds obtained are readily soluble in water, and, in aqueous solutions, prove to be typical electrolytes.

After sulfonium compounds had been discovered [11] numerous representatives of this class of compounds were prepared; nevertheless, the conditions under which they are formed have not been studied enough.

Carrara [12] while studying the rate of formation of triethylsulfonium iodide, found that the reaction was not quantitative under the experimental conditions he used. Ray and Levine [13], showed that for stoichiometric proportions of sulfide and the alkyl iodide, the reaction only went 50% of the way; at the same time complicated side-reactions leading to the formation of hydrocarbons and free iodine were found to occur. Bost and Everett [14] established that formation of sulfonium salts proceeds readily in a methanol medium. Hellstrom [15] showed that the reaction slows down in acid media. It follows from the papers quoted that formation of sulfonium salts proceeds best with methyl iodide in a methanol medium.

The aim of the work described here was to develop a method for the quantitative determination of organic sulfides on the basis of the formation of sulfonium compounds.

On heating a mixture of organic sulfide and methyl iodide in methanol at 100°, in a sealed ampoule, formation of the sulfonium compound proceeds quantitatively. Organic sulfides can be determined by heating a mixture of test samples, containing up to 0.5 millimole of sulfides, with 3-5 ml of methanol and about 5 millimoles of methyl iodide (ten times the expected amount of sulfides) in a thick-walled ampoule at 100° for 2-3 hours. The reaction mixture is then transferred from the ampoule to a separating funnel, and the ampoule rinsed out with water; the washings are added to the reaction mixture in the separating funnel. The unreacted methyl iodide is removed from the aqueous layers, and the aqueous solution extracted first with chloroform and then with ether for extraction of free iodine and methyl iodide residues. The aqueous solution is then transferred to a 250 ml standard flask. 50 ml of this solution is taken for titration and 10 ml of 0.05 N silver nitrate added; the mixture is then heated to the boil. The solution is diluted with water to about 100 ml, when a few mls of concentrated nitric acid is added and the whole boiled again to coagulate the silver iodide.

Excess silver nitrate is finally titrated with 0.05 N ammonium thiocyanate using ferric alum as indicator. In another aliquot of the same solution (50 ml), the hydrogen iodide formed is determined by titration with 0.05 N sodium hydroxide, using methyl red as the indicator. The organic sulfide sulfur content is calculated by means of the formula:

$$\% S_{\text{sulfide}} = \frac{0.05(a - b) \cdot 32.07 \cdot 5 \cdot 100}{100 \cdot K},$$

where a is the amount of 0.05 N silver nitrate used up, in mls; b is the amount of sodium hydroxide used up, in mls; and K is the weight of the sample taken, in g.

Results for the determination of various individual organic sulfides are given in Table 1.

TABLE 1

Determination of Individual Sulfides

Sulfides	Amount taken, in moles · 10^{-3}	Found		Deviation, in %
		moles · 10^{-3}	in %	
Diallylsulfide	0.756	0.747	98.7	−1.3
		0.749	98.9	−1.1
Diisobutylsulfide	0.420	0.419	99.7	−0.3
		0.421	100.3	+ 0.3
Dipropylsulfide	1.171	1.175	100.2	+ 0.2
		1.176	100.3	+ 0.3
Dibenzylsulfide	0.416	0.417	100.1	+ 0.1
		0.420	100.0	+ 1.0

Thiophene, thianthrene, and diphenylsulfide do not give sulfonium salts.

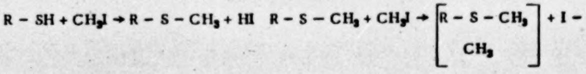
Results for the determination of organic sulfides in gasolines are given in Table 2.

TABLE 2

Determination of Organic Sulfides Added to Gasolines

Composition of the mixture	Amount taken, in moles · 10^{-3}	Found		Deviation, in %
		moles · 10^{-3}	in %	
Petroleum-cracking gasoline and dipropylsulfide	0.1888			
Diallylsulfide	0.0494			
Diisobutylsulfide	0.0596			
Total:	0.2978	0.2971	99.8	−0.2
Fraction of shale gasoline 145-160°, and dipropylsulfide	0.1461			
Diallylsulfide	0.0781			
Diisobutylsulfide	0.0491			
Total:	0.2733	0.2682	98.4	−1.6

Anosile, guaiacol, and tricresol do not affect determination of organic sulfides. The method does not give correct results in the presence of mercaptans. In this case, more complicated reactions occur, e.g.:



$$R-SH+CH_3I \rightarrow R-S-CH_3+HI \quad R-S-CH_3+CH_3I \rightarrow \left[R-\underset{CH_3}{S}-CH_3\right]+I^-$$

Accordingly, for determination of organic sulfides by the method described it is necessary to remove mercaptans beforehand.

SUMMARY

A method has been developed for the determination of organic sulfides, which is based on the formation of sulfonium salts with an alkyl iodide.

It has been shown that this method can be used for the determination of individual organic sulfides in the presence of unsaturated and oxygen-containing compounds.

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DETERMINATION OF KETONES, ESTERS, AND ACIDS IN THE PRODUCTS OBTAINED BY LIQUID-PHASE OXIDATION OF PARAFFIN HYDROCARBONS, ON THE BASIS OF THEIR ABSORPTION SPECTRA IN THE INFRARED

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Chemical methods of analyzing the products from the liquid-phase oxidation of paraffin hydrocarbons are fairly complicated, and, in individual cases, particularly for the oxidation products of high-molecular hydrocarbons, analysis for ketones and esters does not always give correct results. Accordingly, we have studied the possibility of using infrared spectroscopy for the quantitative analysis of such mixtures. The published methods [1-2] of functional analysis of mixtures of oxygen-containing derivatives on the basis of their absorption spectra in the infrared have a number of drawbacks; they are either not accurate enough or are only applicable in the absence of carboxylic acids. The latter circumstance does not permit the use of these methods for the analysis of the oxidation products of unsaturated hydrocarbons, the acid content of these oxidation products, as a rule, being high.

In the work described here we have tried to develop a method for the quantitative determination of ketones, esters, and acids which would be reasonably accurate, and rapid to carry out, such as that required for kinetic studies, and also for the practice of oxidation of high molecular weight hydrocarbons of the paraffin series.

The spectra were registered on an IKS-11 apparatus with a sodium chloride prism. The apparatus was provided with a setup for automatically operating the slit, and also included an amplifier for registering the spectra by means of the EPP-09 recorder [3]. The cuvettes were of a type that prevented evaporation of the solvent during registration of the spectra [4]. The accuracy of determination of the position of bands in the 1700 cm^{-1} region was ± 3 cm^{-1}.

Calculation of the concentration C was carried out on the basis of the Lambert-Beer equation, the applicability of which was checked for all derivatives; $C = D/Kl$, where D is the optical density ($D = \text{logarithm}\ (I_0/I)$).

Here the intensity I_0 of the ray passing through the solvent is found by a method described earlier [4]; I is the intensity of the ray passing through the test solution; 1 is the thickness of the cuvette. The value of K was determined without taking into account apparatus corrections, so that it is necessary when working with other apparatus to carry out preliminary calibration with the test materials used. The materials whose spectra were taken were of varying origins:

a) Acetone, methyl ethyl ketone, dibutyl ketone, ethyl acetate, amyl acetate, and butyric and stearic acids were the commercial products purified by distillation or recrystallization.

b) Stearone was synthesized [5] from stearic acid, and was purified by a threefold crystallization from alcohol; m.p. 86.4° (published value 88.4°).

c) Methyl stearate was synthesized [5] from commercial stearic acid, and was purified by distillation under vacuum.

d) The synthetic fatty acids of varying composition were mixtures mainly of normal carboxylic acids containing small amounts of isocarboxylic acids; they were obtained by oxidation of mixtures of high-molecular weight paraffins at the SZhK combine in Shebenko. Various fractions of these acids were used; these fractions were obtained both by fractional distillation and by precipitation as their urea complexes. The composition of the fraction is approximately determined by the distillation range.

e) The methyl esters of the synthetic acids were prepared by using the cation exchange resin PFSK [6], and were purified by fractional distillation.

TABLE 1

Class of material	Name	Molecular weight	Absorption coefficient, k, $m^{-1}cm^{-1}$	Band width, in cm^{-1}	Frequency cm^{-1} ν	Solvent
Ketones	Acetone	58	310	15	1719	CCl_4
	Dibutylketone	142	310	17	1716	Heptane
	Methyl ethyl ketone	72	290	18	1722	CCl_4
	Heptanone-2	114	290	16	1719	CCl_4
	Stearone	508	320	14	1715	$CHCl_3$
	Mixture of ketones in oxidized paraffin (saponified)	–	–	18	1719	CCl_4
	Ketones (mixture)	249	280	17	1718	CCl_4
Esters	Ethyl acetate	88	520	–	1740	CCl_4
	Amyl acetate	130	486	14	1740	CCl_4
	Ethyl capronate	144	500	–	1744	Cyclohexane
	Ethyl stearate	298	500	14	1742	"
	Methyl esters of mixed acids $C_{14}-C_{16}$	338	511	20	1740	"
	Esters of C_{13} alcohol and $C_{14}-C_{16}$ acids	432	488	18	1736	"
Acids	Butyric acid	88	820	14	1712	Heptane
	n-Valeric acid	102	790	15	1712	CCl_4
	Stearic acid	284	780	14	1712	CCl_4
	Normal acid $C_{10}-C_{16}$	243	820	14	1709	CCl_4
	Normal acid $C > 21$	330	820	–	1709	CCl_4
	Mixture of acids $C_{10}-C_{18}$	247	670	18	1713	CCl_4
	Mixture of acids $C_{14}-C_{16}$	228	677	–	1713	CCl_4
	Mixture of acids C_7-C_9	156	700	16	1711	CCl_4
	Mixture of acids C_5-C_9	133	729	16	1714	CCl_4
	Mixture of "iso" acids $C_{10}-C_{16}$	206	583	21	1714	CCl_4
	Mixture of "iso" acids $C > 21$	266	640	21	1713	CCl_4

f) Esters of the synthetic fatty acids and C-13 alcohol: C-13 alcohol is the designation for a mixture of primary alcohols obtained by hydrogenation, by means of Adkins'[7] catalyst, of a narrow fraction of the methyl esters of the synthetic acids. The mean equivalent weight of these alcohols is 198; this corresponds to an alcohol with 12.9 atoms of carbon. The esters of this alcohol and the fatty acids from the C-14 and C-16 fractions were prepared by esterification in the presence of the cation exchange resin PFSK, and were purified by distillation under high vacuum.

g) Ketones (mixtures) with a mean molecular weight of 249 were obtained by oxidation of VZHS secondary alcohols with chromic anhydride, with subsequent purification and distillation under high vacuum.

The characteristics of the test materials used are given in Table 1.

Let us consider analysis in the presence of materials containing one > C = O group in the mixture.

For the purposes of quantitative functional analysis it is possible to use those absorption bands which preserve their characteristic frequency in a homologous series, and also exhibit constant absorption coefficients. Published results [8-9] as well as our own, permit one to conclude that the absorption bands of the carbonyl groups of ketones, esters, and acids, satisfy these requirements to a considerable extent. The absorption band for the C=O group in aliphatic ketones has a frequency of 1718 ± 3 cm^{-1}, while for the esters and acids the frequencies are respectively 1738 ± 3 cm^{-1} and 1713 ± 2 cm^{-1}.

The absorption coefficients which we established (Table 1) indicate that they are constant within the group of acids, esters, and ketones, since changes in their value do not exceed ± 2.5-3% of the mean value. When one bears in mind that during the analysis of mixtures the experimental errors for all the components will be meaned it can be considered that variations in the absorption coefficients will give an error less than this.

In the case of one of the simplest cases of functional analysis of mixtures consisting only of esters, acids, or ketones, the molar extinction of such a mixture will be somewhat different from that of an individual compound. We shall find the value of this difference which is introduced because of incomplete agreement with respect to the frequencies of the carbonyl bands of the components of one homologous series.

The absorption coefficient of the carbonyl band for a mixture of materials can be calculated if the contours of the bands of the individual materials are known.

It has been shown that for many compounds, the contour of the carbonyl band is described quite well by the Lorenz equation [10]

$$D = \frac{a}{(\nu - \nu_0)^2 + b^2}. \tag{1}$$

where ν_0 is the band frequency at the maximum; ν is the frequency of contour point; a and b are constants; and D is the optical density.

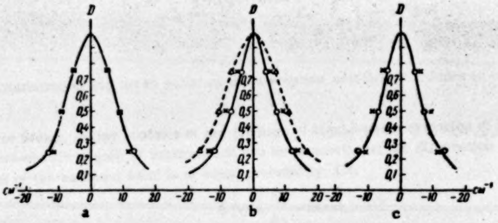

Fig. 1. Contours of the absorption band of the > C= O bond (values determined from the spectrograms):
a) Methyl ethyl ketone; ●) individual methyl ethyl ketone;
x) ketones in oxidized paraffin (values found from the spectrograms);
b) stearic acid; o) individual stearic acid; ×) $C_{10}-C_{18}$ acids;
Δ) contour of $C_{10}-C_{18}$ "iso" acids; c) methyl stearate; Δ) individual methyl stearate; ×) esters of C_{13} alcohol and $C_{14}-C_{18}$ acids.

The contours which we obtained by means of the IKS-11 apparatus for the carbonyl bands of ketones, esters, and acids, are also satisfactorily described by this equation with constants which are constant within each group of materials. In Fig. 1 are shown the contours of carbonyl groups calculated by means of equation (1) and calculated from the spectrograms. Optical density is plotted along the ordinate – the optical density at the maximum being taken as unity – while the width of the contour, in reciprocal centimeters, is plotted along the abscissa.

From equation (1), and using the Lambert-Beer law, we gets

$$K = \frac{\alpha}{(\nu - \nu_0)^2 + b^2} \quad (2) \quad \text{where} \quad \alpha = \frac{a}{Cl}$$

Let us assume further that we have n + 1 materials with equal absorption coefficients, for which the position of the carbonyl bands is displaced relative to one another by the same amount equal to $\frac{\Delta\nu}{n}$, and that all the bands are located in the frequency range $\nu_0 - \frac{\Delta\nu}{2}$, $\nu_0 + \frac{\Delta\nu}{2}$. At the point ν_0 the optical density of the total absorption band will be given by:

$$D = \sum_i D_i = l \sum K_i C_i,$$

where K_i is the absorption coefficient of the i'th band at a frequency of ν_0; C is the concentration of each component.

The total absorption coefficient K is determined from the equation:

$$l \Sigma K_i C_i = K_0 l \Sigma C_i ,$$

from which the absorption coefficient of the mixture is given by $K_0 = \Sigma K_i C_i = \frac{1}{C_0} \Sigma K_i C_i$.

Since, during liquid-phase oxidation of high-molecular weight hydrocarbons, a wide selection of compounds with various functional characteristics is obtained, in order to obtain K_0 in an integral form, we shall consider the case where n → ∞. For this purpose, we shall determine the distribution function of the concentration of the materials according to the frequencies of the carbonyl band:

$$C_\nu = \varphi(\nu) d\nu.$$

Here, $\varphi(\nu)$ is the distribution function, and C_ν is the molar concentration of the components of the mixture in which the frequencies of the carbonyl bands lie within the limits ν, $\nu + d\nu$, then

$$K_0 = \frac{1}{C_0} \sum K_\nu \varphi(\nu)\, d\nu = \frac{1}{C_0} \int\limits_{\nu_0 - \frac{\Delta\nu}{2}}^{\nu_0 + \frac{\Delta\nu}{2}} \frac{a\varphi(\nu)\, d\nu}{(\nu - \nu_0)^2 + b^2}.$$

Thus, determination of the mean value of the absorption coefficient reduces to establishing the distribution function $\varphi(\nu)$.

As tests have shown, during analysis of the products of liquid-phase oxidation of high-molecular weight paraffins with a reasonable degree of accuracy, it can be assumed that the distribution of components according to the frequencies of the carbonyl band is of equal probability, i.e.

$$\varphi(\nu) = \frac{C_0}{\Delta\nu} = \text{const},$$

then

$$K_0 = \frac{1}{\Delta\nu} \int\limits_{\nu_0 - \frac{\Delta\nu}{2}}^{\nu_0 + \frac{\Delta\nu}{2}} \frac{a\, d\nu}{(\nu - \nu_0)^2 + b^2}$$

By integrating, and resolving into series, we get:

$$K_0 = \frac{2a}{b\Delta\nu} \operatorname{arctg} \frac{\Delta\nu}{2b} = \frac{2a}{b\Delta\nu} \left[\frac{\Delta\nu}{2b} - \frac{\Delta\nu^3}{24b^3} + \cdots\right] = \\ = \frac{a}{b^2} \left[1 - \frac{\Delta\nu^2}{12b^2} + \cdots\right] = K \left[1 - \frac{\Delta\nu^2}{12b^2} - \cdots\right], \qquad (3)$$

where K is the absorption coefficient of an individual material. For $\Delta\nu = 5\ \mathrm{cm}^{-1}$ and $\underline{b} = 8\ \mathrm{cm}^{-1}$, we get

$$K^* = K\left(1 - \frac{2.5}{64} - \frac{1}{512}\cdots\right) = 0.962\,K.$$

Thus, for the values of K we are considering: they can be expressed with a reasonable degree of accuracy by just the first two members of the resolution, and even in this case, the total absorption coefficient of the mixture will only differ by 1% from the absorption coefficient of an individual material. It is obvious that for any other form of the distribution function of the concentrations of the components, as long as it is symmetrical with respect to point ν_0, and does not have a minimum (this is usually fulfilled), the difference between K_0 and K will be even smaller.

TABLE 2

Test material	K-absorption coefficient, in $M^{-1}L\ cm^{-1}$	$K_{calc.}$ $M^{-1}L\ cm^{-1}$	b, in cm^{-1}	$\Delta\nu$, cm^{-1}
Ketones	300	288	9	6
Esters	500	470	7	6
Acids	780	755	7	4

Table 2 contains the values for the absorption coefficients of ketones, esters, and acids, meaned for several individual compounds calculated according to formula (3), and also the values of $\Delta\nu$ and $\underline{b}$; the latter remain constant in each series of functional derivatives.

During the oxidation of certain types of natural paraffin, in addition to acids with a normal structure, up to 30% of "iso" acids [11, 12] are formed, the carbonyl group of which has a lowered value for the absorption coefficient (Table 1) and a widened band contour (Fig. 1). At the same time the absorption coefficients of acids with "normal structure", isolated from the mixture of oxidation products, have values similar to those of the absorption coefficients of individual acids, and their contour coincides with the contour of stearic acid. As a consequence of the presence of "iso" acids, all the mixture of acids formed during oxidation has an absorption coefficient which is lower than the value determined by means of formula (3). This fact must be borne in mind when analyzing mixtures with appreciable amounts of "iso" acids.

In order to carry out an analysis, a sample of material $\underline{m}$ is dissolved in a known volume of CCl_4 or cyclohexane. The volume of solvent is chosen so that the optical density of the carbonyl band lies within the limits 0.3-0.6, in order to ensure the minimum experimental error. The optical density in the maximum of the band is found from the spectrograms taken in the 1700-1750 cm^{-1} region, while the molar concentration of material in the solvent (C) is calculated by means of the Lambert-Beer equation. The concentration C of the carbonyl-containing material in the original mixture is calculated by means of the equation:

$$C_n = \frac{C\nu}{m}\ \text{millimoles/g}, \tag{4}$$

where C is the concentration in the solvent, and ν is the volume of solvent.

Determination of the concentration of ketones in the oxidation products of hydrocarbons is usually complicated when acids are present, since the absorption band of the carbonyl group of the acids is superimposed on the absorption band of the ketones. Analysis, is, however, possible, if, after determination of the optical density of the carbonyl band at the frequency of the ketone carbonyl group, a correction is made for absorption arising out of the presence of the carbonyl group of the acids.

Actually, for two superimposed absorption bands, we have:

$$D_{total} = D_{K-T} + D_K\,,$$

from which

$$C_K = \frac{D_{total}}{K_K l} - \frac{K_{K-T}}{K_K}\,C_{K-T}\,. \tag{5}$$

Here K_K is the absorption coefficient of the ketone carbonyl band at the maximum point of this band, while K_{K-T} is the absorption coefficient of the carbonyl group of the acids at the same frequency; C_K and C_{K-T} are molar concentrations. Analysis of materials in cases where there occurs superposition of bands is fairly common in spectroscopic practice. This problem is most easily solved when the contours of the superimposed bands are known. In our case the band contours are described quite well by the Lorenz equation, right up to distances from 15-20 cm^{-1} from the center of the band. Since the distance between the centers of the carbonyl bands of ketones and acids is, on an average, equal to 5 cm^{-1}, the equation is used in order to determine the correction factor. At the band center, when $\nu = \nu_0$, we have

$$K_{\text{мах}} = \frac{a}{b^2}.$$

Dividing equation (2) by this expression, we get:

$$K/K_{\text{мах}} = \frac{1}{1+\left(\frac{\nu-\nu_0}{b}\right)^2}. \tag{5a}$$

We then place

$$K/K_{\text{мах}} = \eta; \qquad \frac{\nu-\nu_0}{b} = \zeta,$$

whence

$$\eta = \frac{1}{1+\zeta^2}. \tag{6}$$

Formula (6) is the equation for the contour in dimensionless coordinates, the origin of which is related to the center of the band. The frequency shift from the center of the band, expressed in b units, is an independent variable, and is nothing else but the half-width of the contour at the point $D = D_{\max}/2$. For mixtures of acids, $b = 9\ \text{cm}^{-1}$, while the distance from the center of the band to the maximum point of the ketone band is equal to 5 cm^{-1}. Consequently, $\eta = 0.75$. $K = 585\ \text{m}^{-1}\text{L}\ \text{cm}^{-1}$ at the maximum of the ketone band.

Having registered the spectra of the mixture of ketones and acids in CCl_4 solution (or other suitable solvent), and having found D_{total} from equation (5), the concentration is calculated; the acid content is determined beforehand by titration of the mixture, while acid content in the carbon tetrachloride is determined by calculation. The content of ketones in the original mixture is finally calculated by means of equation (4).

The absorption coefficient of the acids is considerably smaller than that of the ketones; this lowers the accuracy of the analysis when large concentrations of acids are present. Accordingly, it is interesting to know the ratio of the concentation of acid to ketones, for which it is expedient to carry out an analysis.

From equation (5), we have:

$$\Delta C_{\text{к}} = \frac{\Delta D_{\text{total}}}{K_{\text{к}} l} + \frac{K_{\text{к-т}}}{K_{\text{к}}} \Delta C_{\text{к-т}}. \tag{7}$$

Assuming that the error in determining C_{K-T} by titration is 3%, while the error in determining the optical density ΔD is equal to 0.005, we can find what should be the ratio C_{K-T}/C_K so that the ketone can be determined with an accuracy of up to 10%. For a value of $D = 0.5$ for the optical density of the ketone band, the first member in expression (7) does not exceed 1%, when the total error is of one order higher. Disregarding this, therefore, we get:

$$0{,}1 C_{\text{к}} = \frac{K_{\text{к-т}}}{K_{\text{к}}} \cdot 0{,}03\ C_{\text{к-т}}$$

or

$$C_{\text{к-т}} = 1.70\, C_{\text{к}},$$

i.e., in order to determine ketone concentration with an accuracy of up to 10%, the concentration of acid in the mixture should not exceed that of the acetone by more than one and a half times.

For the determination of the concentration of ketones and esters when present together, analysis reduces to a calculation of the mutual correction for the superposition of the bands of the compounds. The carbonyl bands of esters have a frequency of 1738 ± 3 cm^{-1}, while those of the ketones have a frequency of 1718 ± 3 cm^{-1}; the distance between these bands is equal to 20 cm^{-1} on the average. The absorption coefficients of ester carbonyl in the ketone region, and on the other hand of ketone carbonyl in the ester region, can be found by means of equations (5a) and (6). Using equation (5) which is applicable in the given instance, we have:

$$C_{\text{к}} = \frac{D_{\text{к}} - \eta_E K_E C_E l}{K_{\text{к}} l} \qquad C_{\text{к}} = \frac{D_{\text{к}} - \eta_E D_E}{K_{\text{к}} l}$$

$$C_E = \frac{D_E - \eta_{\text{к}} K_{\text{к}} C_{\text{к}} l}{K_E l} \qquad C_E = \frac{D_E - \eta_{\text{к}} D_{\text{к}}}{K_E l}.$$

Here C_K, C_E, K_K, and K_E are the concentrations and absorption coefficients of ketone and ester respectively; l is the cell thickness; D_K and D_E are the optical densities of the carbonyl bands in the ketone and ester regions respectively. Solving these equations, we get:

$$C_{\text{к}} = \frac{D_{\text{к}} - \eta_E D_E}{K_{\text{к}} l (1 - \eta_E \eta_{\text{к}})}; \qquad C_E = \frac{D_E - \eta_E D_{\text{к}}}{K_E l (1 - \eta_E \eta_{\text{к}})}. \tag{8}$$

The product $\eta_E\ \eta_K$ is approximately 0.025; accordingly, if the order of accuracy required is not too high, this value can be disregarded with respect to unity.

During determination of ketones and esters in each other's presence it is desirable that their absorption bands should be resolved on a spectrogram. The ketone and ester bands are resolved by the IKS-11 apparatus fitted with an NaCl prism for a spectral slit width of 9 cm^{-1}, when the optical density of one band is not more than twice that of the other. In addition, the optical density should not be more than 0.3. This ratio of the optical densities was checked by us on synthetic mixtures, and also by means of spectrograms of oxidized paraffins. In Fig. 2 are given the resolution of ketone and ester bands for mixtures of oxidized paraffins, as well as the values of their optical densities.

In the case of the analysis of highly-oxidized paraffins, when appreciable amounts of acids are formed, for increasing the experimental accuracy of the determination of ketones and esters it is best to remove the acids or to convert them into salts. The carbonyl band is strongly shifted to the lower frequency side (down to 1560 cm^{-1}) in the spectra of the carboxylic acid salts. This opens up the further possibility of determining ketones and acids in the presence of acids, since, by converting the latter into salts by neutralization with alkali, it is then possible to eliminate mutual superposition of the carbonyl bands almost completely. The analysis can then be carried out as described above.

TABLE 3

Concentration in mole/liter, according to the Infrared Spectra

Ketones	Esters
0.45	0.26
0.47	0.24
0.50	0.29

Various methods can be used according to the nature of the test material:

1. For the analysis of samples of oxidized high-molecular weight paraffins, it is best to neutralize and partially remove the acids by converting them into their salts. This is carried out by dissolving a test sample in a mixture of water and alcohol (1 : 1) and neutralizing it with alcoholic KOH to the phenolein endpoint. A known volume of cyclohexane, heptane, or other suitable solvent is then added to the contents of the flask; the flask is strongly shaken and sealed with a ground glass stopper; after separation of the layers, a few mls of the upper layer is pipetted out. After drying for

TABLE 4

Oxidation product	Acid No. of oxidate	Determination, N	conc'n. per infrared spectra in moles/1	
			ketones	esters
Oxidate No. 1				
a) Neutralized with KOH	33	1	0,49	0,293
b) Saponified with KOH by boiling for 2 hr; extract. with petroleum ether		2	0,47	
c) Partially titrated to acid number 10.7		3	0,48	0,288
Oxidate No. 2				
Oxidized paraffin	110	1	0,193	0,92
		2	0,190	0,89
Oxidate No. 3	23	1	0,17	0,170
		2	0,20	0,20

TABLE 5

Composition of mixture	ketone conct., in moles/ liter		ester conct., in moles/ liter		Solvent
	wt. of synth. mix. taken	as found by infra-red	wt. of synth. mix. taken	as found by infra-red	
Methyl stearate Methyl ethyl ketone	0,0652	0,0634	0,0615	0,0615	Cyclohexane
Esters from $C_{10}-C_{16}$ acids and C_{13} alcohols	0,0288	0,0284	0,0201	0,0209	Cyclohexane
Esters of $C_{14}-C_{16}$ acids and C_{13} alcohols Methyl ethyl ketone + $C_{14}-C_{18}$ acids	ketone 0.0310 acid 0.0199	—	0,0467	0,0464	Cyclohexane
Esters of $C_{14}-C_{16}$ acid and C_{13} alcohols. Ketones (mixture) mol. wt 249.	0,01620	0,01625	0,00790	0,00745	CCl_4

TABLE 6

Oxidate	ketones, in moles/1.		esters, in moles/1.	
	ketones, moles/1	by chem. analy.	ketones moles/1	by chem. analy.
Oxidate No. 1, oxidized paraffin	0,48	0,50	0,290	0,290
Oxidate No. 1, partially neutralized to acid number 10.6	0,46	0,48		
Oxidate No. 1, neutralized	0,42	0,435		
Oxidate No. 2, a. No = 10.7			1,67	1,40
Oxidate No. 3			1,47	1,28
Oxidate No. 4			0,456	0,44
Oxidate No. 5			1,21	0,92

a short time with a small amount of $MgSO_4$, the spectrum of the solution obtained is registered and the ketone content determined by means of formula (4). During extraction of the neutralized sample with cyclohexane some of the salts formed may be taken up in the cyclohexane layer; this, however, as indicated above, should not affect the accuracy of the method. A basic source of error could be the transfer of the ketones or other carbonyl-containing compound into the aqueous-alcohol phase. All the same, during analysis of oxidized paraffin, these errors amount to less than 0.5%, since after a supplementary extraction of the aqueous-alcohol phase with cyclohexane, no ketones are found in the latter. Table 3 shows the reproducibility for determination of ketones and esters by means of their infrared spectra after removal of acids, followed by extraction with cyclohexane; the test material was oxidized paraffin with an acid number of 33.

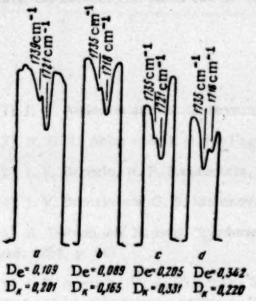

Fig. 2. Absorption bands of the > C = O group of ketones and esters in oxidized paraffins (IKS-11 apparatus).

2. In those cases where extraction is undesirable for some reason or other, the following procedure is adopted: a sample of the test mixture is dissolved in a few milliliters of absolute alcohol with gentle warming, and the solution neutralized with alcoholic KOH. The alcohol is then removed by evaporation under vacuum, or by heating; the residue is dissolved in a known volume of CCl_4, after which the spectra are registered. A large part of the acid salts remains in the precipitate. This sequence of operations, can, of course, only be followed when one can be sure that no ketones or esters will be lost.

For the analysis of solid oxidized paraffins, the following method is also suitable: an aliquot of the oxidized paraffin is neutralized with 0.1 N alcoholic KOH in an aqueous-alcohol (1 : 1) mixture with preliminary warming until the whole sample has dissolved. The precipitate is filtered off and dried in air, together with the filter paper. An aliquot of this precipitate is dissolved in carbon tetrachloride or some other suitable solvent, and the spectra of the carbonyl group resistered; the concentrations of ketones and esters are then calculated.

Table 4 contains results which characterize the reproducibility of this procedure. For oxidate No. 1 results are given for the concentration of ketones and esters when the test material was treated in three different ways with alkali: 1) complete removal of acids; 2) partial removal of acids until an acid value of 10.6 was obtained; 3) saponification by boiling in normal KOH for 2 hours on a water bath.

In those cases where a rapid but not-so-accurate determination is required of the concentration of ketones and acids, and where removal of acids is not resorted to, use can be made of the absorption coefficients which have been corrected for mutual superposition of the bands.

Table 5 contains results for the analysis of synthetic mixtures; experimental accuracy amounts to ± 3-6 %.

We have also carried out a large number of determinations of ketones by the hydroxylamine-pyridine method [13] for control purposes. The results obtained by both methods are in satisfactory agreement with each other. The small, systematic difference between the results obtained by the hydroxylamine method and those obtained by the infrared method, can, in our opinion, be related to the presence of high-molecular weight ketones which do not react completely with hydroxylamine.

The generally accepted method of estimating esters in an oxidized sample is their saponification by heating with alkali followed by titration with acid. The values for ester concentration given in Table 6 were determined by this method.

The ester values found by saponification are higher than those found by the infrared method. There seem to be no systematic regularities in these deviations.

In conclusion we should like to express our thanks to N. K. Man'kovskii for his gift of samples of oxidized paraffins and acids for the work.

SUMMARY

It has been shown that it is possible to determine ketones and esters in mixtures of oxidation products and paraffins on the basis of the absorption spectra of the $>C=O$ bond.

Absorption coefficients and band contours have been measured for individual materials, and for mixtures of carbonyl-containing materials, by means of the IKS-11 apparatus. The effect of the shift in the frequencies of the components of the mixtures on the extinction coefficients of the absorption bands of the mixtures has been established.

The values of the corrections to be applied to the absorption coefficients, when ketones, esters, and acids are all present together, have been determined. Methods are described for removing the acids so that the accuracy with which the ketones and esters can be determined is increased.

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COLOR REACTIONS OF NITROINDANEDIONE

COMMUNICATION II. REACTIONS WITH INDOLES AND CARBAZOLE*

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2-Nitroindanedione-1,3 $[C_6H_4=(CO)_2=CH \cdot NO_2]$ gives a series of color reactions with organic compounds [1], which can be used for the qualitative detection of these compounds. Of these reactions, those with pyrroles are particularly valuable. Pyrroles give red or orange colors with nitroindanedione both in aqueous and in alcoholic and acetic acid solutions; the color appears without application of heat. Heating usually enhances the sensitivity of the reaction. Thus, pyrrole gives a red color with nitroindanedione which can be detected at a dilution of 1 : 200,000, while on heating it can be detected at a dilution of 1 : 3,333,000. With N-methylpyrrole a red color can be observed at a dilution of 1 : 333,000 in the cold, while on heating the color can be observed at a dilution of 1 : 10,000,000.

In this connection it appeared interesting to investigate the behavior of compounds containing the pyrrole ring condensed with other rings. The reactions of nitroindanedione with indoles and carbazole form the subject of the work described here.

Colors Given with Nitroindanedione (in Alcoholic, Acetic Acid, or Aqueous Solutions)

Test material	Color of the solution observed	Limiting dilution at which a color can still be observed	
		Without heating	After heating
Indole	Red	1 : 333,000	1 : 333,000
N-Methylindole	Red	1 : 125,000	1 : 250,000
2-Methylindole	Orange to violet	1 : 100,000	1 : 100,000
3-Methylindole (skatole)	Orange	No color	1 : 50,000
7-Methylindole	Red	1 : 500,000	1 : 5,000,000
2,3-Dimethylindole	Orange to violet	On heating in glacial acetic acid	
2,3-Diphenylindole	Orange to red	On heating in glacial acetic acid	
Carbazole	Orange	No color	1 : 20,000

Indole and its homologs give very intense colors with nitroindanedione, these colors frequently appearing without applying heat. When a drop of a dilute alcohol solution of indole is added to a saturated aqueous solution of nitroindanedione, a red color appears almost immediately. The limiting dilution at which this red color can still be observed is 1 : 333,000. Heating, in the case of very dilute indole solutions, speeds up the appearance of the color somewhat, but the reaction sensitivity does not increase. When the indole solutions are not very dilute, a red precipitate is obtained, particularly on heating.

Of the indole homologs tested, 7-methylindole (see Table) exhibits the highest reaction sensitivity with nitroindanedione. A red color is observed; at the limiting dilution the color is, however, orange. The reactions of N-methylindole, and of 2-methyl- and 3-methylindole (skatole) with the reagent are less sensitive.

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* For Communication I see Bull. Acad. Sci. Latvian SSSR, No. 10 (87), 143 (1954).

When an aqueous or alcoholic solution of nitroindanedione is heated with heteroauxin (3-indoleacetic acid), then only after 15 minutes does a weak orange color appear. A solution in glacial acetic acid, however, on boiling, gives a red color after one minute. The reaction has a low sensitivity; it is possible that heteroauxine itself does not give a color, but that a color is given by its decomposition products (e.g. products formed by decarboxylation) which may be formed on boiling.

2-3-Dimethylindole initially gives a greenish color which gradually changes to violet, when it is reacted with an aqueous solution of nitroindanedione. On heating, the color becomes an intense red; further prolonged boiling changes the color to brown and a red precipitate formed. In alcoholic solution a greenish-violet color is observed at first, but this changes to red. In glacial acetic acid, on heating, an orange color is very rapidly observed. The sensitivity is low.

2,3-Diphenylindole does not give a color with nitroindanedione in aqueous solution, but in alcoholic and in glacial acetic acid, on heating, an orange color is first observed which changes over to red. The reaction sensitivity is low.

Some samples of petroleum contain porphyrins [2]. Pyrroles and indoles would also be expected to be present in petroleum in addition to porphyrins. It was actually found that petroleum gives colors which are characteristic of indoles and pyrroles when tested with nitroindanedione.

When one or two drops of Bakinskii petroleum is diluted with alcohol or glacial acetic acid, and some nitroindanedione added, and the mixture then allowed to stand for some time or heated for a few minutes, a red, red--violet, or violet color appears. The same effect can be obtained by shaking Bakinskii petroleum with alcohol or glacial acetic acid and adding nitroindanedione to the filtrate.

Carbazole, on heating with nitroindanedione in alcoholic solution, gives an orange color. The limiting dilution is 20,000.

It has been shown previously [3] that 2-bromo-2-nitroindanedione-1,3 also gives a number of color reactions with pyrroles, indoles, and carbazole; the highest reaction sensitivity is exhibited by carbazole while the least sensitive reactions are those with indoles and pyrroles. The reaction between bromonitroindanedione with tryptophane is very characteristic; nitroindanedione, however, does not give a color with tryptophane. Thus, both reagents can supplement each other.

The reaction is carried out by adding nitroindanedione, either in the solid form or in solution, to a test solution in alcohol, glacial acetic acid, or water, and shaking the whole. When indoles (and pyrroles) are present, a color appears rapidly; this color is usually red or violet-red; at high dilutions the color is orange. When no color is observed, the solution is heated. The appearance of a color only after heating for some time indicates a very low concentration of indoles or pyrroles, or indicates the presence of indoles substituted in the 2 and 3 positions, or the presence of carbazole.

SUMMARY

2-Nitroindanedione-1,3 gives characteristic colors in alcoholic, acetic, or aqueous solutions with indole, its homologs, and carbazole. With indoles the color usually develops without application of heat.

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*Original Russian pagination. See C. B. Translation.

DETERMINATION OF MIXTURES OF XYLENE AND ETHYL-BENZENE ISOMERS

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Chemical methods of analyzing the isomeric composition of technical xylene, despite the appearance of spectrographic methods, are still fairly widely used, since they ensure satisfactory accuracy, and do not require complicated apparatus. The method based on sulfonation of xylene followed by separation of the sulfonic acids or their salts [1-4], gives large errors, particularly during determination of the contents of o-xylene and ethylbenzene. Determination of xylene isomers by oxidizing them into the corresponding dicarboxylic acids, and determination of ethylbenzene by its oxidation to benzoic acid [5,6] lead to losses which are difficult to assess during oxidation, particularly during separation of the acids; as a consequence, it has been suggested that this mixture of acids should be analyzed by an X-ray method [7]. Some authors have converted the mixture of xylene isomers into the trinitro derivatives with subsequent determination of the latter [8-13]. This method permits determination of meta- and para-xylene, and total o-xylene and ethylbenzene with reasonable accuracy.

The technique which we have developed permits quantitative determination of all three xylene isomers and ethylbenzene; it is based on nitration of the mixture of xylene isomers, and determination of the trinitro derivatives according to the method published earlier [14], coupled with quantitative separation by efficient fractionation of o-xylene which boils 5.3° higher than m-xylene, which is the isomer which has the boiling point nearest to it [15].

Determination of o-xylene.* The original technical xylene consisted of a mixture of the three isomeric xylenes and ethylbenzene, and did not contain more than 1% non-aromatic hydrocarbons;** it was fractionated for removal of the o-xylene, using a column of 33 theoretical plates and a reflux ratio of not less than 15 : 1. The fractions boiling up to 139.5° were almost free of o-xylene; all the latter remained in the residue. The o-xylene content of the bottoms was determined from the temperature of crystallization, using the fusion diagram for the system o-xylene—m-xylene; on the basis of this result, the content of the o-xylene in the original xylene was then determined.

TABLE 1

Determination of o-Xylene

o-xylene taken		o-xylene found		Relative error, in %
in g	in %	in g	in %	
30.0	15.0	29.4	14.7	−2
30.0	15.0	28.8	14.4	−4
50.0	25.0	50.0	25.0	0
60.0	30.0	58.5	29.3	−2.3

We were of the opinion that the impurity most likely remaining with the o-xylene in the bottoms would be m-xylene, since the latter has the boiling point which is nearest to that of o-xylene. In view of the comparatively small volume of the bottoms during analysis of technical xylene, the error arising out of the possible presence of small amounts of other isomers, which is a consequence of such an assumption, is insignificant.

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* N. E. Khromova-Borisova and N. G. Borzova took part in the experimental work.

** When the test sample contained an appreciable amount of non-aromatic hydrocarbons, they were removed beforehand by azeotropic distillation with methanol [17].

Results are given in Table 1 for the determination, by the method described, of o-xylene in synthetic other mixtures containing the other isomers.

Determination of m-Xylene, p-Xylene, and Ethylbenzene. The fraction of xylene boiling up to 139.5°, and which was free from o-xylene, was nitrated to give trinitrotoluenes in two stages: in the first stage the xylene was nitrated to the dinitro state, while the second stage consisted of converting the dinitro compounds to the trinitro derivatives.

First Stage: 5 g of xylene was placed in a nitration flask provided with a stirrer, a reflux condenser with a groundglass joint, a dropping funnel, and a thermometer.

While the xylene was stirred and the temperature kept at not more than 40° on a water bath, a nitrating mixture of the following composition was added dropwise to the contents of the flask: 61-62% sulfuric acid, 20-25% nitric acid, and 13-14% of water; the nitrating activity factor was 75-76.,* The amount of nitrating mixture taken was such that the amount of nitric acid present was 10% in excess of that theoretically necessary.

When all the nitrating acid had been added, the temperature was gradually increased to 90-95°, and kept at this temperature for one hour, the mixture being stirred continuously. The contents of the nitration flask were then allowed to cool to room temperature; the nitrated product was isolated from the waste acid and subjected to further nitration.

Second Stage. To the fused dinitro product heated to 60-70° was added with stirring a second mixture of acids containing 80-81% sulfuric acid, 13-14% of nitric acid, and 5-6% of water; the nitrating activity factor in this case was 88-89. The amount of nitrating mixture taken was such that the amount of nitric acid present was 65% in excess of the theoretical amount (for nitration from dinitro to trinitro). When all the nitrating mixture had been added, the final mixture was kept at 100° for 30 minutes, and for 2 hours at 120°, the mixture being agitated continuously. The contents of the nitration flask were then cooled to room temperature and poured into 5-6 times their volume of cold water. After settling, the diluted acid was decanted through a tared Nutsch filter with a No. 3 and No. 4 sintered glass disc. The trinitro product remaining in the flask was washed 3 times with cold water and twice with hot (60-70°) water, using 100 ml portions each time. The wash water was decanted through the same filter. When washing with hot water, the contents of the flask were cooled again to 20-25° before decanting off the wash water. All the trinitro product was transferred onto the filter by means of the last lot of wash water; the trinitro product was squeezed free of water (not too strongly, to avoid loss of the oily part) and dried to constant weight at 60°. Filter plus trinitro product were then weighed and the total yield of the trinitro derivatives of m-, p-xylene, and ethylbenzene determined.

The nitrated ethylbenzene, which is considerably more soluble in alcohol than the trinitro derivatives of m- and p-xylene [16], was removed by washing the nitrated product on the filter with ethanol in 10 ml portions, the product being thoroughly mixed with the alcohol on the filter and the wash alcohol then sucked off. Completion of the washing process was established by the absence of oily drops of the nitroproduct on evaporating a few drops of the wash alcohol on a watch glass. 7 washings were usually enough.

The filter, together with the nitro product which had been treated as described above with alcohol was then dried to constant weight at 60°; the total yield of trinitrometa- and trinitroparaxylene was then determined. The proportions of these two were established by means of setting points and the appropriate fusion diagram [14].

The oily product soluble in alcohol contains, in addition to trinitroethylbenzene, some incompletely nitrated nitration products of m- and p-xylene; the amounts of these products, under the nitration conditions used, amounted to – according to our results – about 2% of the weight of trinitrometaxylene and about 10% of the weight of trinitroparaxylene. These amounts were taken into account during determination of the amounts of trinitroethylbenzene (see the example given).

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* The nitrating activity factor "F" is calculated by means of the formula [19]:

$$F = \frac{S}{1 - \frac{N}{140}}$$

where S is the sulfuric acid content of the mixture in %, N is the nitric acid content of the mixture in %.

On the basis of the analytical results obtained for the nitration products, the proportions of the various isomers in the xylene taken for nitration were calculated, by making use of the experimental coefficients which we established for the yields of the trinitro products during nitration under identical conditions of the individual xylene isomers, and of synthetic mixtures of these isomers in different proportions. These coefficients, which were established experimentally, are:

for m-xylene — 1.95 (for a m-xylene content of the mixture up to 80%)
for m-xylene — 2.0 (for a m-xylene content of 80-90%)
for m-xylene — 2.1 (for a m-xylene content greater than 90%)
for p-xylene — 1.55
for ethylbenzene — 1.65

Example. Determination of the composition of xylene by the nitration method.

During nitration of 5 g of xylene the following were obtained:

Oily trinitro product	— 9.10 g
Weight of non-oily trinitroxylene after washing	— 6.50 g
Weight of "xylene oil," removed with alcohol by alcohol washing	— 2.60 g

The setting point of the non-oily trinitroxylene was 170.0° which corresponds to a composition of 75% trinitrometaxylene and 25% trinitroparaxylene

Weight of trinitrometaxylene	6.50 · 0.75 = 4.88 g
Weight of trinitroparaxylene	6.50 · 0.25 = 1.62 g
Weight of incompletely nitrated products	
During nitration of m-xylene:	4.88 · 0.02 = 0.1 g
During nitration of p-xylene:	1.62 · 0.1 = 0.16 g
	Total 0.26 g
Weight of trinitroethylbenzene	2.60 g - 0.25 g = 2.35 g

On the basis of the experimental coefficients for the yield of trinitroproducts during nitration, we can now calculate the composition of the original xylene:

Amount of m-xylene in the original xylene taken for nitration 4.88/ 1.95 = 2.5 g, or 50%.

Amount of p-xylene 1.62/ 1.65 = 1.05 g or 21%.

Amount of ethylbenzene 2.34/ 1.65 = 1.42 g or 28.5% = approximately 29%.

Results of the analysis of several synthetic mixtures of m-, and p-xylene and ethylbenzene by the method described above are given in Table 2.

TABLE 2

Analysis of Synthetic Mixtures of m- and p-Xylene and Ethylbenzene

Taken, in g			Found, in g			Relative error, in %		
m-xylene	p-xylene	Ethylbenzene	m-xylene	p-xylene	Ethylbenzene	m-xylene	p-xylene	Ethylbenzene
3.50	1.50	—	3.50	1.55	—	0	+3.3	—
			3.62	1.48	—	+2.9	−0.7	—
3.90	0.60	0.50	3.90	0.63	0.55	0	+5.0	+10
			3.95	0.64	0.53	+1.3	+6.7	+6
1.0	1.50	2.50	0.94	1.55	2.65	−6.0	+3.3	+6
			0.92	1.52	2.70	−8.0	+1.3	+8
—	2.50	2.50	—	2.40	2.60	—	−4.0	+4
				2.48	2.45	—	−0.6	−2
3.75	—	1.25	3.73	—	1.27	−0.3	—	+2
			3.79	—	1.25	+1.3	—	0

Some of the xylene samples analyzed by the method described were also analyzed spectrophotometrically.* Both methods gave results which agreed with each other satisfactorily (Table 3).

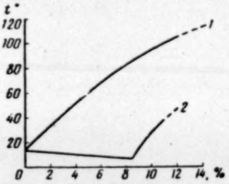
TABLE 3

Comparisons of the Results of the Nitration and Spectrophotometric Methods of Analyzing Xylene

By the nitration method, in %				By the spectrophotometric method, in %			
o-xylene	m-xylene	p-xylene	ethylbenzene	o-xylene	m-xylene	p-xylene	ethylbenzene
21	37	18	24	20	36	19	25
–	47	23	30	–	43	24	33
–	13	18	69	–	11	19	70
17.5	47	19	17.5	17	45	19	19

The method described gives satisfactory results during the analysis of typical samples of technical xylene consisting of mixtures of all the xylene isomers and ethylbenzene. This method can also be used for the analysis of mixtures of m- and p-xylene in any proportions, and for the determination of other xylene isomers present as impurities in m-xylene. In the case of analysis of experimental mixtures of isomers containing a predominating amount of ethylbenzene (50-80%) during nitration very oily, products, which are difficult to filter, are obtained. In order to avoid this, samples with ethylbenzene contents in excess of 40% can be nitrated, by adding a known amount of pure m-xylene to such samples prior to nitration, and then taking the amount of m-xylene added into account during the final calculation.

For the analysis of xylene fractions containing 85% and more of ethylbenzene, the remaining components being m- and p-xylenes,** the method described is not suitable, since the trinitro-products obtained are liquid in form and contain very small amounts of crystals which are difficult to filter from the liquid phase. Addition of m-xylene in order to increase the amount of solid phase in the trinitro products is not applicable either, since in the given instance, it leads to large errors during the determination.



Relation between the temperature of incipient crystallization and the content of trinitrometa- and trinitroparaxylene in trinitroethylbenzene: 1) Trinitrometaxylene; 2) trinitroparaxylene.

For such fractions we have developed another analytical technique: the p-xylene content was determined by means of the temperature of incipient crystallization; the m-xylene content was determined by the nitration method, and the ethylbenzene content was determined by difference.

Determination of p-Xylene. To 3-5 g of test sample was added p-xylene in sufficient amount to bring the crystallization point down below 40°. The temperature of incipient crystallization of this mixture was then determined; from the fusion diagram for the system p-xylene – ethylbenzene [18] the amount of p-xylene in the mixture was then determined. After subtracting the amount of p-xylene added in the first instance, the content of p-xylene in the original xylene was determined. The experimental error in determining p-xylene, when using a low-temperature thermometer with 0.5 divisions, is about 5% absolute.

Addition of p-xylene is necessary to avoid too low temperatures and to prevent overcooling of the system.

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* The spectrophotometric analysis was carried out in the physical laboratory of the Leningrad Sci. Research Institute of the Ministry of the Oil Industry by A. N. Aleksandrov.

** o-Xylene is absent from these fractions since it is readily removed quantitatively by efficient fractional distillation.

The presence of m-xylene in the test sample does not interfere with determination of p-xylene by the method described, since in this concentration range the depression of the temperature caused by the m-xylene is almost the same as that caused by ethylbenzene [18].

Determination of m-Xylene. A separate aliquot of test sample (5 g) was nitrated to the trinitro product, which was a mixture of trinitroethylbenzene, trinitrometaxylene, and trinitroparaxylene. Nitration and washing were carried out as described above.

The washed nitro-product was dried at 60° to constant weight in the same vessel as that used for washing. The dried product was heated until it was completely liquid when it was poured into a test tube; the latter was placed in an apparatus for determining setting points, the apparatus being heated to a temperature slightly higher then the expected incipient temperature of crystallization. The apparatus was cooled slowly and the temperature at which the contents of the tube started to become turbid (initial separation of solid phase) noted.

The trinitrometaxylene content of the nitro-product was determined by means of a diagram* (Fig. 1, Curve 1) constructed on the basis of the relationship which we established between the temperature of incipient crystallization of the nitro-product and its content in trinitrometaxylene. Then, using the coefficient established experimentally for the yield of trinitrometaxylene during nitration — equal, in the given instance to 1.95 — the m-xylene content of the test sample was calculated.

Example. During nitration of 5 g of a sample of ethylbenzene containing m-xylene, 8.1 g of trinitro-derivative with an initial temperature of crystallization of 96° was obtained; this corresponds to a content of trinitrometaxylene of 10%.

The amount of trinitrometaxylene 0.1 · 8.1 = 0.81 g.

The amount of m-xylene in the original sample = 0.81/ 1.95 = 0.415 g or 8.3%.

The presence of up to 8.5% of trinitroparaxylene in the nitro-product does not affect the temperature at which crystals of trinitrometaxylene separate out, as the result of the formation of melts of trinitroparaxylene and trinitroethylbenzene with a low temperature of incipient crystallization and an eutectic at a content of 8.5% of trinitroparaxylene (Fig. 1, Curve 2). For trinitroparaxylene contents in excess of 8.5%, it crystallizes from the melt (as the component in excess when compared with the composition of the eutectic) at the same temperatures as those at which it crystallizes from the same melt of trinitrometaxylene (see Fig. 1, Curve 2); accordingly trinitrometaxylene cannot be determined on the basis of the temperature of incipient crystallization of the nitro-product. In this case, in order to decrease the concentration of the p-xylene in the test sample, pure ethylbenzene should be added in known amounts to the sample; the synthetic mixture thus obtained should then be analyzed as described above, and the amount of ethylbenzene added originally taken into account during the calculation.

TABLE 4

Determination of Small Amounts of m-Xylene in Ethylbenzene

m-Xylene taken		m-Xylene found		Relative error, in %
in g	in %	in g	in %	
0.2	2.0	0.163	1.63	−8.0
0.18	3.6	0.17	3.4	−5.6
0.5	5.0	0.51	5.1	+2.0
0.5	5.0	0.52	5.2	+4.0
0.4	8.0	0.415	8.3	+3.8
0.8	8.0	0.73	7.3	−8.8
0.8	8.0	0.76	7.6	−7.0
1.0	10.0	0.91	9.1	−9.0

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* The setting point of pure trinitroethylbenzene is 37° [20]. Technical dinitroethylbenzene is liquid at room temperature. The technical product obtained by nitration of ethylbenzene to the trinitro derivative, as we showed experimentally, contained 4-5% of dinitroethylbenzene, and this depressed the setting point to 14-15°.

Results for the determination of the m-xylene content of synthetic mixtures by means of the method described are given in Table 4.

In view of the low absolute values of the m-xylene being determined, the relative error is fairly considerable, but the absolute error does not exceed 1%.

SUMMARY

1. A method is suggested for the analysis of technical xylene in which all the xylene isomers are determined, together with the amount of ethylbenzene present; the method consists of fractional distillation for removal of o-xylene, followed by nitration in conjunction with phase analysis for the determination of m-xylene, p-xylene, and ethylbenzene.

2. A method has been developed for determination of the isomeric composition of xylenes and ethylbenzene in mixtures with a high content of ethylbenzene (upwards of 85%).

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CHROMATOGRAPHIC SEPARATION OF RHENIUM AND TUNGSTEN

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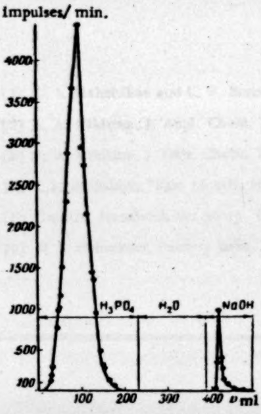
Rhenium and molybdenum exhibit a large difference in their capacity to be absorbed on the anion exchange resin EDE-10 from phosphoric acid media [1]. Sexivalent molybdenum forms a heteropoly compound with phosphoric acid, in which the molybdenum is located in the complex anion which is readily sorbed by the anion exchange resin; rhenium in the septivalent state does not form such compounds, but passes into the filtrate on washing the column with 2 M H_3PO_4. Tungsten also tends to form a heteropoly compound with phosphoric acid, which is similar to those formed between molybdenum and phosphoric acid [2-3]; this permits separation of rhenium from tungsten.



Chromatographic separation of weighable amounts of rhenium and tungsten.

Rhenium is used for coating tungsten wire in filaments [4], and also forms alloys with tungsten which are used in new technical fields. Separation of this pair of elements is therefore of importance for their subsequent determination.

Rhenium was separated from tungsten under dynamic conditions on a column 12 cm long and 6 mm in diameter filled with anion exchange resin EDE-10 in the phosphate form; the particle size of the resin was 100-150 mesh. Synthetic mixtures of W : Re = 1000 : 1; 1 : 1; and 1 : 400 were used for the work. The mixtures were made up from weighable and tracer portions of these elements. The tracers used were the radioisotopes W^{185} and Re^{186}, whose purity was checked radiometrically. 0.1-0.2 ml of the mixture of tungsten and rhenium in the form of sodium tungstate and sodium perrhenate respectively, was introduced into the upper part of the column, and the rhenium eluted with 2 M H_3PO_4. The elution process was controlled by measuring the activity of the Re^{185} in the eluate, and by the color reaction with $SnCl_2$ and KSCN. When all the rhenium had been eluted off the column, the latter was washed with water; the tungsten was then eluted from the column with 10% NaOH. That all the tungsten had been eluted was checked by the absence of activity in the last portions of eluate, and by a negative reaction for tungsten with thiocyanate.

On the basis of the results obtained for the activities of the various portions of eluates, and the changes in intensity of the color of these eluates, an elution curve was constructed for rhenium and tungsten. The separation of tungsten and rhenium for a ratio of one to the other of 1 : 1 is shown in Fig. 1. The curves are similar in character for the other ratios of the two metals. Completeness of elution of Re^{186} and W^{185} was established by summing the activities of the individual portions of eluate, while quantitative determination of weighable amounts of rhenium and tungsten was carried out by means of nitron acetate for rhenium [5], and photometrically, using the thiocyanate reaction for tungsten [6].

W taken		Re taken		Ratio	W found		Re found	
in mg	in impulses/ / minute	in mg	in impulses/ / minute	W : Re*	in mg	in impulses/ / minute	in mg	in impulses/ / minute
	2500	4		1 : 400		2561	4.09	
8		8		1 : 1	8.2		8.07	
4			23040	1000 : 1	4.12			23140

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* The ratios by weight of W : Re were calculated on the basis of the specific activity of the radioisotopes Re^{186} and W^{185}.

The results given in the Table show that rhenium is removed satisfactorily from tungsten by anion exchange.

SUMMARY

A method has been developed for separating rhenium from tungsten on the anion exhcnage resin EDE-10 using 2 M H_3PO_4. Separation of the elements is based on differences in their behavior towards phosphoric acid which forms complex anions with tungsten only; these anions are strongly held by the active groups of the resin.

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*Original Russian pagination. See C.B. Translation.

THE REACTION OF URANIUM WITH FERRON (7-IODO-8-HYDROXY-QUINOLINE-5-SULFONIC ACID)

V. A. Mikhailov

Sexivalent uranium gives with ferron an intense brown color at a pH of 5 in an urotropine buffer. The sensitivity of the reaction when carried out in a volume of 2 ml is equal to 10 γ / ml (limiting dilution 1 : 10^5). No reaction occurs at the same pH in an acetate buffer. Maximum color intensity is observed at pH 4.5-5.5. Using the isomolar series method of Ostromyslenskii - Zhob (at 520 and 360 mμ) it was established that uranium and ferron interact in the molar proportions of 1 : 2 (Fig. 1).

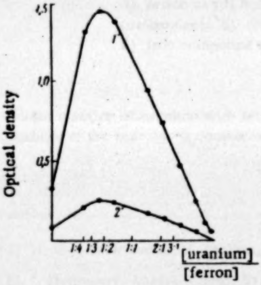

Fig. 1. Determination of the composition of the compound formed between uranium and ferron, using the isomolar series method. pH 5 (urotropine), total concentration of uranium and ferron 1.7 · 10^{-3} mole/ / liter. Reference cell – water. 1) At 360 mμ; 2) at 520 mμ.

During the photometric determination of aluminum [1-2], and during the precipitation of thorium [3] with ferron in an acetate buffer, no formation of the brown color was observed in the presence of uranium.

From the point of view of selectivity the reaction of uranium with ferron is of no great interest. The reagent reacts with trivalent iron [2, 4]. The absorption curves of ferron and of the compounds formed between this reagent and uranium, aluminum, and iron [2] respectively, are shown in Fig. 1. Ferron solution in strongly acidic or alkaline media has a light absorption maximum at 360 mμ, while at pH 4-5 the maximum lies at 340 and 430 mμ (Fig. 2). The compound of ferron with uranium also shows a maximum at 360 mμ. This curve is similar to the absorption curve for ferron in alkaline media, but differs from the latter by its appreciable absorption at 430-600 mμ. The same absorption maximum at 360 mμ is also observed in the case of the compounds formed between ferron and trivalent iron and aluminum. The fact that the position of the light absorption maximum is the same for the reagent itself in alkaline media, and for the compounds which it forms in more acid media (pH 5), leads one to conclude, according to Kuznetsov's hypothesis [5], that inner molecular dissociation occurs here. It is of interest to note that the intensity of this light-absorption band is directly proportional to the number of ferron groups in the molecule, while the mean coefficient E_{360} calculated per mole of ferron is approximately 2300. The occurrence of light absorption in the visible may be related to the chromophoric action of sexivalent uranium [6-7]. This conclusion is confirmed by a consideration of the absorption curves of the compounds formed between ferron and aluminum or iron. The aluminum ion does not exhibit a chromophoric action, while the ferric ion does possess this property. Accordingly, the aluminum compound hardly absorbs at all in the region above 430 mμ, while the iron compound absorbs light in the visible more strongly than uranium, and has an additional maximum at 600 mμ.

Thus, comparison of the absorption curves leads one to conclude that during formation of the compounds of ferron with iron and uranium respectively, the two mechanisms of color formation noted by Kuznetsov [5,6] occur together. The nature of the changes in the curves indicates that iron exerts a stronger chromophoric action than uranium.

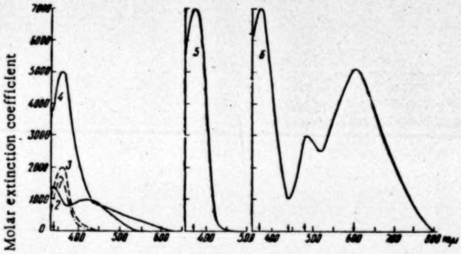

Fig. 2. Absorption curves: 1) Ferron at pH 0; 2) ferron at pH 5; 3) ferron at pH 8-13; 4) compound of uranium with ferron at pH 5 (urotropine); 5) aluminum compound at pH 5 (acetate buffer); 6) iron compound at pH 5 (acetate buffer). Reference cell – water.

SUMMARY

A color reaction of uranium with ferron is described. On the basis of a comparison of the absorption curves, the mechanism of the reaction is considered.

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DETECTION OF MAGNESIUM IONS BY MEANS OF N-ARYLQUINOCYANINE DYES

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A large number of reagents are known for the qualitative detection of magnesium; these reagents interact with magnesium ions to give colored precipitates or colored solutions [1-6].

We have tested N-arylquinocyanine dyes for detecting magnesium. The syntheses of these dyes have been described in the literature [7-9].

All the trimethine quinocyanine dyes with a symmetrical structure (with similar hetero residues at each end of the polymethine chain) which we tested proved to be very sensitive reagents for magnesium ions.

All the dyes studied, both symmetrical and unsymmetrical in structure, are almost insoluble in water, but are readily soluble in ethanol, forming intensely colored solutions; we used their 0.01-0.02% alcoholic solutions. In acid and neutral solutions of magnesium salts, on addition of alcoholic solutions of dyes of symmetrical and unsymmetrical structure, no changes were observed in the colors of the solutions or of the colored precipitates as compared with a "blank". When, however, in the same cases, to 1 ml of a solution of magnesium salt, slightly colored by an alcoholic solution of a trimethinequinocyanine dye with a symmetrical structure, two or three drops of NaOH or KOH solution was added, and intensely colored precipitate was formed.

It must be pointed out that in the case of appreciable concentrations of magnesium in solution, it is best to use, as tests showed, a 0.1 N alkali solution, while for low concentrations the alkali strength should be 2 N solution.

The colored precipitates formed do not decompose on heating the solutions to the boiling point.

Addition of alkali to solutions of magnesium salts, to which an alcoholic solution of a dye with an unsymmetrical structure has been added beforehand, led to the precipitation, for the most part, of colorless magnesium hydroxide.

The table contains results obtained during the study of the interaction between magnesium hydroxide and several symmetrical trimethinequinocyanine dyes.

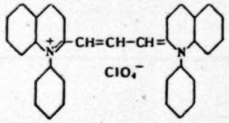
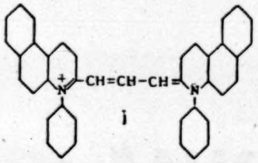
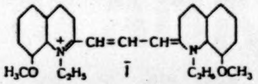
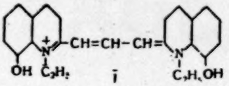
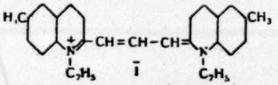
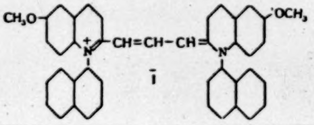
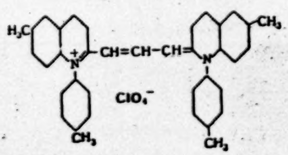
K^+, Na^+, NH_4^+, Ba^{2+}, Sr^{2+}, Ca^{2+} ions do not give colored precipitates, and do not change the color of alkaline solutions of the dyes. For a ratio of magnesium to each of these ions of 1 : 500, there is no appreciable drop in the sensitivity of the reactions for all seven dyes. There is no drop in reaction sensitivity at a ratio of Mg^{2+} : NH_4^+ of 1 : 100. The dye bis-(1-phenyl-5,6-benzoquinoline-2)-trimethinecyanine iodide is particularly sensitive (0.1 γ/ml); the sensitivity of this dye for magnesium ions is considerably higher than that of many known reagents for magnesium (titan yellow, magneson, quinalizarin, triozenes, and hydroxytriazenes, etc.).

Most ions of the fourth and fifth analytical groups interfere with detection of magnesium by means of trimethinequinocyanine dyes, since in alkaline media, hydroxides and basic salts are precipitated which mask the reaction for magnesium; such elements must therefore be removed before detecting magnesium.

For removing interfering ions, the latter are precipitated as sulfides by means of Na_2S under strictly controlled pH values of the test solution.

Procedure for Detecting Magnesium Ions. When the test solution contains free acid, the solution must be neutralized beforehand by adding approximately 0.1 N NaOH dropwise until the appearance of a slight turbidity

Interaction of Trimethinequinocyanine Dyes with Magnesium Ions in an Alkali Solution

Dye	Color of		Limit of identification, in γ/ ml. Limiting dilution
	Alkaline solution of dye	precipitate formed	
	Violet	Red light blue	1 : 500 000
	Light-blue	Dark-blue	0,1 1 : 10 000 000
	Rose	Red-violet	2 1 : 500 000
	Violet	Red-blue	2 1 : 500 000
	Violet	Red	5 1 : 200 000
	Blue	Red-violet	1 1 : 1 000 000
	Violet	Red	1 1 : 10 000 00

which does not disappear; this turbidity is then destroyed by addition of a few drops of 0.1 N HCl.

To 0.5-1 ml of test solution prepared in this way is added 1-2 ml of borate buffer solution (pH 7.60-7.80) and the heavy metals precipitated as their sulfides by dropwise addition of 0.5 N Na_2S. After addition of each drop of sulfide, the contents of the tube are mixed and tests carried out for excess S^{2-}. This is carried out by dipping a capillary pipet for some time in the test solution, and then touching a piece of filter paper moistened beforehand with 1-2 drops of 0.5 N $SbCl_5$ with the tip of the pipet. When precipitation of group III, IV, and V elements is complete, and the minimum amount of Na_2S is present in solution, a clearly discernible orange ring is observed around the tip of the capillary. When it is certain that precipitation of the sulfides is complete, the contents of the test tube are filtered through a close filter paper and the test for magnesium carried out.

2-3 drops of a 0.01-0.02% alcoholic solution of one of the dyes indicated in the table is then added to the filtrate; this is followed by 2-3 drops of 2 N NaOH and the whole mixed; precipitation of a colored precipitate is observed against a white background. The appearance of such a precipitate indicates the presence of magnesium ions.

SUMMARY

It has been shown that some trimethinequinocyanine dyes with a symmetrical structure are highly sensitive reagents for magnesium ions. A method has been developed for detecting magnesium in solutions containing ions of all the five analytical groups, by means of trimethinequinocyanine dyes.

Received April 16, 1957

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DETERMINATION OF ALCOHOLS AND PHENOLS PRESENT AS IMPURITIES IN ORGANOSILICON COMPOUNDS CONTAINING ETHOXY-, METHOXY-, AND PHENOXY-GROUPS

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In order to determine alcohols photometrically we have made use of a reaction which we have described in the literature [1]; this reaction is based on the capacity of alcohols to dissolve $Fe[Fe(SCN)_6]$ with the production of a red color. In addition, we have also suggested a method of determining alcohols present as impurities; this is based on the capacity of alcohols to dissolve the dye methyl violet with formation of a solution with a violet color, while organosilicon compounds containing alkoxy-groups do not dissolve this reagent. $Fe[Fe(SCN)_6]$ was used as the dry powder; the latter was prepared by dissolving 10 g of potassium thiocyanate and 10 g of ferric chloride in separate portions, in 50 ml of absolute methanol.

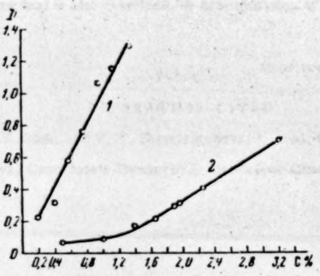

Fig. 1. Calibration curves for determination of alcohol: 1) With $Fe[Fe(SCN)_6]$; 2) with methyl violet.

Solutions of ethanol in tetraethoxysilane were prepared for constructing calibration curves (Fig. 1). To 5-10 ml of these solutions contained in 15-20 ml conical flasks was added about 0.1 g of $Fe[Fe(SCN)_6]$ or methyl violet. The flasks were sealed with stoppers and the contents shaken and then allowed to stand for 20-40 minutes; the solutions were finally centrifuged and the optical density measured on a Pulfrich photometer.

In order to determine the alcohol content of a given sample of tetraethoxysilane or some other organosilicon compound containing ethoxy groups, a known volume of test material was subjected to the same treatment as that used for preparing standards for the calibration curve. The absolute experimental error is 0.01-0.02%, while the relative error is about 1%. The method permits determination of alcohol contents up to the limit of 1.5% when using $Fe[Fe(SCN)_6]$, and from 1.4 to 4-5% when using methyl violet.

The method involving methyl violet has also been tried out with methanol.

Phenol has to be determined in the water extract removed from phenoxysilanes and other organosilicon compounds which are insoluble in water [2]. A ground-up sample of tetraphenoxysilane or phenyltriphenoxysilane containing phenol as impurity was placed in a conical flask and 3-5 ml of water added; the mixture was shaken thoroughly and then centrifuged. To the centrifugate was added 3 drops of 10% $FeCl_3$ solution, or 3 drops of 10% cuprammonium solution. Under these conditions the phenol solution acquired a violet or green color. The optical density of the solutions obtained was finally measured on a Pulfrich photometer.

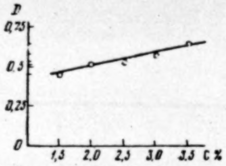

Fig. 2. Calibration curve for determination of phenol with $FeCl_3$.

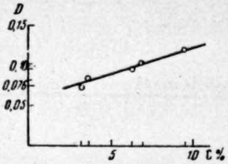

Fig. 3. Calibration curve for determination of phenol by means of the cuprammonium complex.

In order to construct calibration curves (Figs. 2 and 3) aqueous solutions of phenol were prepared. When $FeCl_3$ is used, the limit of identification is 0.05% of phenol, while when the cuprammonium complex is used the limit of identification is 0.15%. The relative error in both cases amounts to 0.7-1.4%.

SUMMARY

Photometric methods are described for the determination of ethanol and methanol present as impurities in organosilicon compounds; a method is also described for determination of phenol as an impurity in the same compounds.

Received January 9, 1957

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* Original Russian pagination. See C. B. Translation.

SEPARATION OF IRON AND COPPER CATIONS BY PAPER CHROMATOGRAPHY IN THE PRESENCE OF LARGE AMOUNTS OF CARBOHYDRATES

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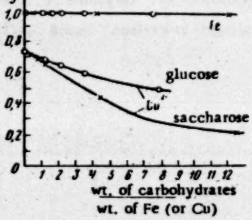
There are well-developed methods in existence at the moment for the paper chromatographic separation of various inorganic compounds, and of a number of organic compounds: carbohydrates, amono acids, etc. [1, 2]. There is, however, practically no published information on the effect of large amounts of organic materials on the chromatographic behavior of inorganic compounds; this is a problem that one often meets in the analysis of foodstuffs.

Of particular interest to us was the study of the effect of carbohydrates (saccharose, glucose) on the chromatographic separation of Fe^{3+} and Cu^{2+}

Amount of carbohydrate, in mg	Ratio carbohydrate / Fe^{3+}	Ratio carbohydrate / Cu^{2+}	R_f Fe^{3+}	R_f Cu^{2+}	Amount of carbohydrate, in mg	Ratio carbohydrate / Fe^{3+}	Ratio carbohydrate / Cu^{2+}	R_f Fe^{3+}	R_f Cu^{2+}
Glucose					Saccharose				
0	0	0	0,98	0,75	0,3	0,22	0,315	0,98	0,75
1,05	0,79	1,11	0,98	0,68	1,1	0,82	1,16	0,98	0,66
2,0	1,49	2,11	0,98	0,66	4,1	3,06	4,32	0,98	0,43
3,3	2,46	3,48	0,98	0,60	12,0	8,2	12,6	0,98	0,23
7,5	5,60	7,90	0,98	0,49					

The behavior of ferric and cupric ions during chromatographic separation in media free from carbohydrates has has been thoroughly studied [3], while the R_f values of cupric and ferric ions in various solvents are known. One of the carbohydrates which we studied – glucose – has reducing properties [4], while the other – saccharose – does not possess these properties [5].



Effect of glucose and saccharose on the R_f values of ferric and cupric cations.

Ferric and cupric ions were separated by ascending chromatography [2] on paper from the Volodarskii factory. The solvent used was a mixture of acetone – hydrochloric acid – water in the proportions 87 : 8 : 5. During separation of ferric and cupric ions by means of mixtures of different composition, i.e., with mixtures of acetone, acid, and water in the proportions 87 : 10 : 3, 87 : 7 : 6, and 87 : 5 : 8, the results obtained were not so well-defined. The R_f value found for iron was 0.98, while that for copper was 0.75; these results are in good agreement with the published values [3]. The chromatograms were developed by spraying with ammonium sulfide [2].

Chromatographic separation of ferric and cupric ions in the presence of carbohydrates was carried out as follows: a drop of an iron solution was placed on a sheet of chromatographic paper and the spot dried out; after drying, a drop of a copper solution was placed on the same place and the drying process repeated; finally a drop of carbohydrate solution of a given concentration was placed on the same spot. The sheet was dried again and a chromatogram run using the same solvent mixture as that indicated above. Replicate chromatograms were run for each test concentration of glucose and saccharose.

The presence of glucose and saccharose in large amounts (Table 1) has no effect on the mobility of ferric ions. Within the limits of experimental error, in all cases $R_f = 0.98$. Thus, Fe^{3+} does not interact with glucose and saccharose (iron was used as a solution of $FeCl_3$).

Glucose and saccharose, however, strongly affect the mobility of cupric ions. In the presence of these carbohydrates the migration rate of the copper drops significantly, the drop being greater the higher the carbohydrate concentration (Fig. 1).

Saccharose exhibits a stronger slowing-up effect than glucose.

We should like to point out that both in the absence of carbohydrates, and in their presence, in all tests, the chromatographic zones for the ferric and cupric ions were quite clearly defined after development with ammonium sulfide. It is probable that in the presence of glucose and saccharose, there is a change in the value of the partition coefficient for the cupric ion between the mobile and immobile solvents, while the partition coefficient for ferric ions, presumably, remains unchanged.

The experiments described above show that it is possible to use the paper chromatographic method for separating Fe^{3+} and Cu^{2+} cations, and for determining them in solutions of saccharose and glucose. Identification of the cations on the basis of the R_f value is only possible in the case of Fe^{++}. In the case of copper it is essential to bear in mind the slowing action of the carbohydrates.

SUMMARY

It has been shown that large amounts of glucose and saccharose do not affect the mobility of trivalent iron cations, but decrease the mobility of copper ions to a considerable extent. Saccharose decreases the mobility to a greater extent than glucose.

Received April 24, 1957

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DETECTION OF URANYL IONS

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A method which has been published in the literature [1] for the detection of uranyl ions in the presence of appreciable amounts of foreign ions (Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO_3^-, MoO_4^{2-}, etc.), on checking has proved to be unreliable: when potassium ferrocyanide was added to the solution, in many cases, there appeared colored precipitates which prevented one from deciding conclusively whether uranium was present or not. Other methods [2, 3] have not attained practical importance.

After several preliminary tests we succeeded in developing a method for detecting uranyl ions in solution containing Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ce^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Be^{2+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO_3^-, MoO_4^{2-}, WO_4^{2-}.

To 2-3 ml of the test solution is added an equal volume of a 10% solution of Complexon III in order to keep most of the metal ions in solution; concentrated ammonia solution is then added until the solution has an ammoniacal odor (if, on addition of ammonia an appreciable amount of precipitate is not formed, it is recommended that some beryllium be added in the form of a solution of one of its salts in order to serve as a collector); the mixture is next heated to the boiling point at which temperature it is kept for two to three minutes; it is finally filtered. The precipitate on the filter, which may contain, in addition to ammonium diuranate, the hydroxides of beryllium, titanium, antimony and some manganese, is washed with hot water until a completely colorless wash liquor is obtained. The precipitate on the filter is treated with a hot 10% solution of sodium carbonate or ammonium carbonate (2-3 ml), the filtrate being passed two or three times through the same filter in order to get more complete solution. During this treatment uranium passes into the filtrate. To one portion of the filtrate is added a drop of a 30% solution of hydrogen peroxide. The rapid appearance of a yellow color indicates the presence of uranium in solution (when sodium carbonate is used for treating the precipitate, chromium may partly dissolve but the chromate color does not appear immediately; uranium can be detected in the presence of chromium at a ratio of uranium to chromium of 1 : 1000); the use of ammonium carbonate at this stage in the presence of large amounts of chromium gives a reaction which is completely reliable.

To another portion of filtrate is added some solid sodium carbonate, and 2-3 drops of potassium ferrocyanide, and about 0.5 ml of 2N HNO_3 added carefully along the wall of the vessel; in the presence of uranium a brown ring is formed at the surface of contact between the sodium carbonate solution and the acid.

The method permits detection of 10^{-5} g/ml of uranium (limiting dilution 1 : 100, 000) in the presence of large amounts of other elements.

SUMMARY

A method has been developed for detecting uranyl ions in a solution containing Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ce^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Be^{2+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO_3^-, MoO_4^{2-}, WO_4^{2-}. The method permits detection of 10^{-5} g/ml of uranium (limiting dilution 1 : 100,000) in the presence of large amounts of other elements.

Received April 25, 1957

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CHRONICLE

THE CONFERENCE HELD AT IVANOVO ON METHODS OF STUDYING COMPLEX FORMATION IN SOLUTION

A conference was held at Ivanovo from the eighteenth to the twenty-first of February which was devoted to discussions of the methods used for studying complex formation in solution. More than 200 delegates attended the conference, among them scientific workers from Moscow, Leningrad, Kiev, Kazan, Kishinev, Kharkov, Alma-Ata and other cities. Thirty reports were read at the seven sessions. The conference was opened by Academician I. I. Cherniaev. His opening speech was followed by I. V. Tananaev's report on "Methods of determining the composition of compounds formed in solution," and also the report by V. N. Tolmachev on "Some limitation of the isomolar series method." In his report, A. K. Babko set forth the principles of the methods of titrating and taking logarithms used for determining composition. V. I. Kuznetsov drew attention, in his paper, to the necessity of studying the changes in chemical reactivity of groups in organic compounds which enter into the composition of complex compounds.

K. B. Iatsimirskii's report was devoted to the complicated, and hitherto comparatively little studied hydrolytic polymerization of metal ions in solution. The report of I. I. Alekseeva (in conjunction with K. B. Iatsimirskii) was devoted to polymeric compounds of molybdenum. In the discussion that followed, the arbitrary character of the term "polymerization" was noted, as well as the necessity for studying the structure of polymers, and taking into account the role of the anions.

A. K. Babko examined experimental methods for determining the dissociation constants of complex groups in solution. N. P. Komar' gave a critical review of methods of calculating successive instability constants (Bjerrum, Leden, etc.) and noted the necessity of making wider use of the method of least squares for calculating the instability constants. A. K. Babko and others who participated in the discussion, pointed out the possibilities of using simpler methods including graphical methods. N. P. Komar' noted the appearance of published papers dealing critically with Bjerrum's concepts of the existence of step-like complex formation in solution.

Other reports which proved of considerable interest were those of A. P. Zozuli (in conjunction with V. M. Peshkova) on the use of the partition method for studying the stability constants of complex thorium compounds, and the report by B. D. Berezin on the study of the solubility of metal phthalocyanine complexes. A new technique for carrying out spectrophotometric studies of complex compounds was recommended by L. P. Adamovich. In his report, A. A. Grinberg gave results on the formation of solution of hitherto unknown complex compounds of divalent palladium, with a coordination number greater than 4.

K. B. Iatsimirskii (together with V. D. Korableva) discussed the use of the theory of the crystalline field for studying certain complexes. The study of complex formation by means of dielectric constants and polarization was the subject of the report by I. A. Sheka and Z. A. Sheka (together with N. E. Kriss). T. N. Sumarovka dealt with the use of the cryoscopic method. V. F. Toropova discussed the possibilities of the polarographic method for studying complex compounds in solution.

At the final session a number of papers were read which dealt with studies of the effect of the solvent on complex formation in solution. Some examples of equilibrium studies in non-aqueous solutions were given in reports by Ia. A. Fialkov, A. V. Ablov, Ia. I. Tur'ian and in communications by B. N. Tolmachev, A. M. Golub, and A. G. Muftalov.

V. P. Vasil'ev made an attempt to calculate the constants for formation of aquo-complexes.

V. A. Mikhailov

CONFERENCE ON POLAROGRAPHIC METHODS OF ANALYSIS

(21-23 January 1958, Kishinev)

The conference on polarographic methods was convened at the instigation of the Analytical Chemistry Department of Kishinev University, the Analytical Chemistry Laboratory of the Moldavian Branch of the USSR Academy of Sciences, and the Kishinev Section of the Mendeleev Society. Scientific workers from Moscow and Dnepropetrovsk participated in the conference in addition to workers from Kishinev. 18 reports were read at the conference, 12 of which were given by workers in Kishinev scientific-research institutions, while the other 6 were given by scientists from Moscow and Dnepropetrovsk.

Several reports dealt with theoretical questions of polarographic analysis (S. I. Siniakova, Ia. I. Tur'ian, A. N. Pushniak, M. B. Bardin, Iu. S. Lialikov, A. A. Gabovich, A. M. Gabovich, and V. M. Bobrinskii).

A number of reports were devoted to the practical application of polarographic analysis and to amperometric titration (N. A. Ezerskaia, V. S. Temianko, Iu. I. Usatenko, V. I. Reznik, E. F. Danilenko and F. M. Tiulinpa; B. V. Lipis, S. Ia. Raik, F. P. Vaintraub, R. M. Novik).

All the reports were heard with great interest and led to lively discussion.

THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION II. THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF PALLADIUM*

Iu. A. Bankovskii and A. F. Ievin'sh
Institute of Chemistry, Academy of Sciences, Latvian SSR, Riga

Of a fairly large number of color reactions which have been described in the literature for palladium, only a few of them have been studied in sufficient detail.

The ease with which palladium is reduced to the elemental state, and the formation, during this reduction, of intensely colored colloidal solutions, have served as the basis for developing a number of methods for detecting and determining palladium [1-7]. Some methods are based on measurement of the optical density of colored complexes of palladium [8-13]. Because of their comparatively low sensitivity, these methods are only suitable for the determination of considerable amounts of palladium.

Methods which are based on the use of organic reagents would seem to be more promising. The reagents most widely used are those which contain the p-nitrosophenylamino group which is characteristic for palladium.

Of this class of reagents, the ones which have found widest application are p-nitrosodiphenylamine [14-15] and p-nitrosodimethylaniline [16-17]. The big disadvantage of these reagents is the effect of neutral salts on them, and the necessity of carrying out a preliminary removal of palladium from Fe, Ni, Co, Cu, Ir, Rh and other elements. For the photometric determination of palladium the following reagents have also been recommended: thiourea [18], 2-mercapto-4,5-dimethylthiazole [19], β-furfuraldoxime [20], α-nitroso-β-naphthol [21], Complexon III [22], methylglyoxime; dimethylglyoxime, salicaldoxime, β-hydroxynaphthaldoxime [23], etc. A review of photometric methods of determining palladium has been given in the paper by Beamish and McBryde [24].

The following reagents have been suggested for the gravimetric determination of palladium: α-furildioxime [25, 26], violuric acid [27], 3-hydroxy-1,3-diphenylhydrazine [28], 4-isopropyl-1,2-cyclohexanedioxime [29], thiobarbituric acid and phenylthiourea [30], dimethylglyoxime [31-33], α-benzoinoxime and β-furfuraldoxime [25], methylbenzoylglyoxime [31], and diethyldithiophosphoric acid [34].

Fuller information on the methods used for the qualitative and quantitative determination of palladium is to be found in a number of reviews [35, 36].

Thiooxime (8-mercaptoquinoline) is a highly specific reagent for palladium; this reagent, under certain conditions, permits the determination of palladium in the presence of other elements; it interacts with divalent palladium ions to form a bright-red 8-mercaptoquinolate (thiooxinate) of palladium which is insoluble in water, the formula of this compound is $Pd(C_9H_6NS)_2 \cdot H_2O$; it is soluble in various organic solvents to give solutions with an intense rose or orange color [37].

The best extractants for palladium thiooxinate are chloroform, chlorobenzene, and bromobenzene. Palladium thiooxinate is less soluble in carbon tetrachloride, diethyl ether, amyl acetate, and carbon disulfide, while it is completely insoluble in aliphatic hydrocarbons.

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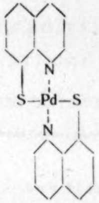
*Communication I, see J. Anal. Chem. 13, 267 (1948).

The ready solubility of palladium thiooxinate in most organic solvents, the high color intensity of these solutions, and the high stability toward acids, give a basis for assigning the structure of an inner-complex salt to this compound.



In accordance with current ideas on the properties of organic reagents of the type R–SH [38], and in view of the presence of a favorable atomic group in the thiooxine molecule, one can postulate the formation of a highly-stable five-membered ring during the interaction of palladium with thiooxine, in which the palladium, while substituting the hydrogen of the mercapto group, is simultaneously connected through a coordination bond with the nitrogen of the pyridine nucleus of quinoline. Palladium thiooxinate possesses a very high stability.

Fifty γ of palladium in the form of an aqueous solution (5 ml) was introduced into a separating funnel, followed by 40 ml of a buffer solution of a definite pH, and 4 ml of a 5% alcoholic solution of thiooxine. The palladium thiooxinate was extracted with 10 ml of chloroform by vigorous shaking for 3-4 minutes. The chloroform extract was filtered through a plug of cotton wool and the color measured in a 1 cm cell in a Pulfrich photometer. The amount of palladium extracted was then determined by means of a calibration curve (in weakly acid solutions) constructed beforehand.

As is evident from Fig. 1, complete extraction of palladium thiooxinate is observed from strongly acid (4 N HCl) solutions. Palladium thiooxinate is also completely extracted from strongly alkaline solutions.

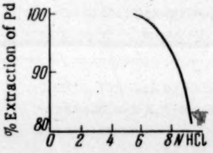


Fig. 1. Extractability of palladium thiooxinate as a function of the acidity of the medium.

It is clear from Fig. 2, that there are three maxima on the absorption curve for a solution of palladium thiooxinate in chloroform, these maxima are at 272 mμ, 286 mμ, and 485 mμ. The molar extinction coefficients of palladium thiooxinate were found to be E_{272} = 43,500; E_{286} = = 39,200, and E_{485} = 7,750. Thus, the highest sensitivity is observed at 272 mμ and also at 286 mμ.

In the work described here, quantitative determination of palladium was carried out in the visible part of the spectrum using a Pulfrich photometer.

As Fig. 3 shows, extracts of palladium thiooxinate in chloroform conform to the Lambert – Beer law up to concentrations of 27 γ/ml (6 N HCl).

More than 5-6 γ of Pd can be determined on a Pulfrich photometer. A spectrophotometer set at 485 mμ permits the determination of as little as 2 γ Pd in the test solution.

Thiooxine, as a reagent which contains the sulfhydryl group, should, according to current ideas [38], react in aqueous media only with those elements which form sulfides which are stable in the presence of water. As a consequence of this, even very high concentrations of the alkali, and the alkaline-earth metals, as well as Al, Ti, Zr, Hf, Th, Cr, etc. do not interfere with determination of palladium. In strongly acid solutions (6 N HCl), in the presence of thiourea (for masking Os, Ru, Pt, Cu, Ag, Au, and Hg) thiooxine is a special reagent for palladium.

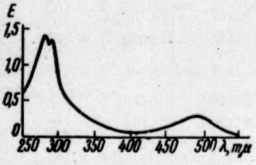


Fig. 2. Absorption spectrum of a 0.000033 M solution of palladium thiooxinate in chloroform (cell 1 cm). Taken on a SF-4 spectrophotometer.

Pt, Os, and Ru react with thiooxine in fairly acid solutions also, and, in rather overwhelming amounts (with respect to palladium), lead to high results for palladium. Platinum in amounts of 20 mg, and osmium and ruthenium in amounts of 1-2 mg, can be masked with thiourea. Iridium and rhodium do not react with thiooxine in strongly acid solution. We have successfully determined Pd (20 γ) in the presence of 2 mg of Rh and 10 mg of Ir. The effect of higher concentrations of Rh and Ir has not been studied.

The effect of the following elements has also been studied: Fe, Co, Ni, Ag, Au, Hg, Zn, Cd, Pb, Mn, Tl, Sn, W, Mo, Sb, Bi, U, As and Ge. With the exception of molybdenum, these elements do not interfere with determination of palladium, even when they are present in amounts which are far greater than that of palladium.

Trivalent iron does not interfere with palladium determination in 6 N HCl when the iron is present in amounts up to 80 mg. Larger amounts (up to 200 mg) can be reduced by sodium hyphophosphite or some other suitable reducing agent (in dilute solutions palladium is not reduced to the metal by hypophosphite) and can be masked by addition of 15 ml of a saturated solution of oxalic acid.

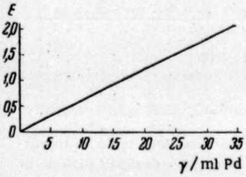


Fig. 3. Conformity of chloroform solutions of palladium thiooxinate to the Beer law (Pulfrich photometer, spectrofilter S-47).

Cu, Hg, Ag, and Au (just like Ru and Os) react with thiooxine in strongly acid solutions. The thiooxinates of Ag and Au are not extracted by organic solvents and do not interfere with palladium determination. When, however, very large amounts of copper are present, some may pass into the extract. Accordingly, Cu like Hg, Ag, and Au (the bulky thiooxinates of which, although insoluble in chloroform, still interfere with the separation of the extract from the aqueous phase) must be masked with thiourea. When thiourea is used for this purpose, 50 ml of test solution (6 N HCl) should not contain more than 2 ml of a 8% solution of thiourea.

In the presence of more than 5-6 mg of Hg, Ag, and Au, the thiooxinates of these elements are precipitated, and though they are not extracted by organic solvents, they still interfere with the separation of the extract from the aqueous phase. In this case, after the extraction has been carried out in a separating funnel, 5-10 ml of a 8% thiourea solution is added, and the whole shaken up. The thiooxinates of these elements thereupon dissolve and the chloroform extract is readily removed.

In the presence of more than 0.5 mg of univalent mercury and divalent tin, low results are obtained for palladium.

Molybdenum (> 20 γ) is the only element that can cause serious difficulties. In the presence of large amounts of molybdenum, it is possible to utilize the lower stability of its thiooxinate as compared with that of palladium, and it can be washed out of the chloroform extract with hydrochloric acid. When 5 mg of molybdenum is present, the extract has an intense brown color. This brown extract is transferred to another separating funnel in which it is shaken up with 60 ml of 8 N HCl for 5-7 minutes. When this is done, the molybdenum thiooxinate is broken down and the chloroform extract assumes the pure rose color of palladium thiooxinate. When 5-7 minutes extraction by vigorous shaking is not sufficient to remove the last traces of brown color, the extract is shaken up once again with another 60 ml lot of 8 N HCl. The extract is then filtered and the extinction measured; palladium is then determined by means of the calibration curve.

There is still one more limitation to the given method for palladium. It is desirable that no oxidizing agent be present. In principle, oxidizing agents do not prevent determination of palladium, but, by oxidizing the thiooxine, they may lead to low results during palladium determination. In view of the high hydrochloric acid concentrations used in the method, the presence of appreciable amounts of nitrates in the test solution is inadmissible. It is best to reduce vanadate to vanadyl, trivalent iron to the ferrous state, etc. This is, however, not obligatory, since thiooxine itself is a reducing agent, and all that will happen in such cases is that more of the thiooxine will be used up.

Determination of Palladium in the Presence of Various Elements (20 γ Pd taken)

Foreign element (Me), in mg	Ratio $\frac{Pd}{Me}$	Pd found, in γ	Foreign element (Me), in mg	Ratio $\frac{Pd}{Me}$	Pd found, in γ
Pt^{IV} — 20	1 : 1000	21	Ge^{IV} — 100	1 : 5000	21
Os^{VIII} — 2	1 : 100	20	Mn^{II} — 560	1 : 2800	19
Ru^{III} — 1	1 : 50	21	Tl^{I} — 70	1 : 3500	20
Rh^{III} — 2	1 : 100	19	As^{III} — 100	1 : 5000	18,5
Ir^{IV} — 10	1 : 500	19,5	As^{V} — 100	1 : 5000	19,5
Cu^{II} — 5	1 : 250	21	Sb^{III} — 50	1 : 2500	21
Ag — 20	1 : 1000	19	Bi^{III} — 50	1 : 2500	21
Au^{III} — 100	1 : 5000	18	Pb — 250	1 : 12500	20
Hg^{II} — 100	1 : 5000	20	Sn^{IV} — 0,5	1 : 25	19
Fe^{II} — 200	1 : 10000	20,5	Se^{IV} — 20	1 : 1000	21,5
Fe^{III} — 80	1 : 4000	21	W^{VI} — 100	1 : 5000	19
Ni — 160	1 : 8000	20	Mo^{VI} — 0,02	1 : 1	22
Co^{II} — 250	1 : 12500	20	U^{VI} — 500	1 : 25000	20
Cd — 400	1 : 20000	20	V^{IV} — 80	1 : 4000	21
Zn — 100	1 : 5000	18,5			

On the basis of numerous experiments a method which is described below has been developed for the determination of palladium. A very large excess of thiooxine (250 mg) with respect to the amount of palladium to be determined is necessary in order to lower the dissociation of palladium thiooxinate at the high acidity used, and in order to ensure its complete extraction. At lower hydrochloric acid concentrations, for example 3 N HCl, it is possible to use only 2 ml of a 4-5% solution of the reagent. For 100% extraction of palladium from 2 N HCl only a very small excess of reagent is necessary. But, at low acidities, a large number of foreign elements interfere.

Analytical Procedure. To not more than 20-25 ml of test solution contained in a separating funnel is added the same volume of concentrated hydrochloric acid, 1.5 ml of 8% thiourea solution, and 5 ml of a 4-5% solution of thiooxine in 6 N hydrochloric acid. Palladium thiooxinate is extracted with 10 ml of chloroform by shaking with the latter for 5 minutes. The extract is removed and filtered through a cotton wool plug: the light absorption of the filtrate is measured in a 1 cm cell in a Pulfrich photometer using a S-47 filter, or on the SF-4 spectrophotometer at 485 mμ. The amount of palladium is then determined by means of a calibration curve constructed under the same conditions using pure solutions of palladium.

When large amounts of iron are present, it should be masked as described above. When more than 20 γ of molybdenum is present it should be subjected to the washing treatment described above.

SUMMARY

1. Paladium thiooxinate $Pd(C_9H_6NS)_2 \cdot H_2O$ is stable in strong acid solutions, and is readily extracted by most organic solvents to give solutions with an intense rose color.

2. A highly specific photometric method has been developed for the determination of palladium (5-270 γ) in the presence of considerably larger amounts of foreign elements such as: Pt, Os, Ru, Rh, Ir, Cu, Ag, Au, Hg, Fe, Ni, Co, Zn, Cd, Ge, Mn, Tl, As, Sb, Bi, Sn, Se, W, Mo, Pb, U, V, etc.

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SEPARATION OF THORIUM FROM TITANIUM, ZIRCONIUM, AND OTHER ACCOMPANYING ELEMENTS BY THE HOMOGENEOUS PRECIPITATION METHOD

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The homogeneous precipitation method[*] has found practical application in analytical chemistry for the determination of calcium [1], barium [2-3], strontium [4-5], lead [6], tin [7], copper and silver [8], thorium [9-11], rare earths [12], nickel and cobalt [8], metals of the hydrogen sulfide group [13-17], and some others. The advantage of this method as compared with ordinary precipitation is well known.

The compounds used as reagents are nonionized compounds which, under conditions leading to hydrolysis, dissociation, or breakdown of complex organic molecules to more simple compounds, supply precipitant ions. Crystallization "centers" (precipitation) are uniformly distributed through the whole volume of the solution. Of the huge number of organic materials which are capable of supplying precipitant ions in solution, few as yet have found application. In particular, methyl- and ethyl oxalates [10, 20] and compounds yielding iodate ions [21] have been suggested for precipitation of thorium. Quantitative separation of thorium as the oxalate in cases where other metal ions are present, is a difficult problem. Thorium oxalate may be obtained either in a gelatine-like form or in the form of coarse crystals [22] depending on precipitation conditions.

For the quantitative determination of thorium it is important to get a precipitate in the form of large crystals; this can be achieved by the homogeneous precipitation method [10].

The reagent which we used for this purpose was acetonedioxalic acid; this was prepared by the condensation of acetone with oxalic acid [23].

$$CO(CH_3)_2 + 2H_2C_2O_4 \rightarrow CO(CH_2COCOOH)_2 + H_2O.$$

Acetonedioxalic acid in aqueous solution provides a precipitant for thorium—the oxalate ion. In aqueous-acetone media the extent of the coprecipitation of accompanying elements decreases, this has been shown to be true in many instances of the precipitation of metal ions from aqueous-organic media [18, 24]. Acetonedioxalic acid should provide large excess amounts of oxalate ions. A large excess of oxalate decreases the extent of the coprecipitation of zirconium and titanium [22], and lowers the solubility product of thorium oxalate [25].

Preparation of a solution of acetonedioxalic acid. Oxalic acid (150-200 g) is dried at 90-100° for 4 hours, after which it is ground, and drying continued for a further 1.5 hours; 40 g of the dried oxalic acid is dissolved in 100 ml of anhydrous acetone (b. p. 56°). The reagent is used on the day following preparation. 15 ml of reagent supplies about 4 g of oxalate ions.

Precipitation of thorium as the oxalate by means of acetonedioxalic acid. Precipitation of thorium as its oxalate has been studied by many authors [21, 22, 26, 27]. Quantitative precipitation of thorium oxalate occurs at a terminal pH of 0.5-2.0 and in the presence of a large excess of oxalic acid; the latter, in addition, decreases the amount of coprecipitation of zirconium and titanium. The presence of a coprecipitant (calcium ions) in solution is essential, since this ensures complete separation of thorium and the rare earths. In the presence of large amounts of foreign ions, and particularly of iron, aluminum, zirconium, and titanium, small amounts of thorium are not quantitatively precipitated as the oxalate. Precipitation of thorium as the oxalate takes 15-18 hours. The presence of other compounds (ammonium salts, phosphates, etc.) in solution prevents quantitative separation of thorium oxalate.

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[*] A. P. Terent'ev and co-workers [18] have suggested the term "the method of in situ nascendi reagents" for such a precipitation. Other authors [9] have called this method "indirect precipitation."

Separation of thorium by means of acetone dioxalic acid in relation to the pH of the solution was investigated as follows.

To 50 ml of solution containing 96.7 γ of thorium, at various pH values indicated in Table 1, 7 ml of acetonedioxalic acid solution was added, and the mixture boiled for 15 minutes. On the following day the precipitate of thorium oxalate was filtered through a "white band" filter paper 7 cm in diameter, and the precipitate washed 2-3 times with 1% oxalic acid; it was then dried and calcined in a 5-6 ml porcelain crucible. The residue was fused with 0.8 – 1 g of sodium peroxide. After cooling, the melt was dissolved on heating in 25 ml of water, the solution was then filtered through a 7 cm diameter "white band" filter paper, and washed 3-4 times with water. The thorium hydroxide on the filter was dissolved in hot 0.09 N hydrochloric acid, and thorium determined by means of arsenazo [28], using a method published previously [29].

TABLE 1

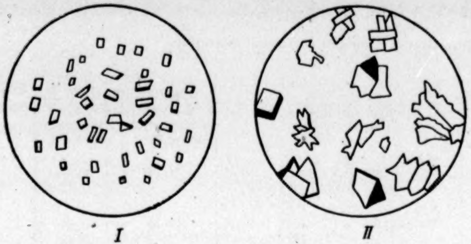
Precipitation of Thorium as Its Oxalate from a Homogeneous Solution (96.7 γ of Th taken)

pH at the end of the precipitation	Th found, in γ	Error in Th, γ	pH at the end of the precipitation	Th found, in γ	Error in Th, γ	pH at the end of the precipitation	Th found, in γ	Error in Th, γ
0.3	71.7	– 25.0	1.5	91.0	– 5.7	2.1•	99.0	+ 1.3
0.6	93.7	– 3.0	1.6	82.0	–14.7	2.6•	97.0	+0.3
0.7	91.2	– 5.5	2.2	58.5	–38.2	3.0•	78.0	–18.7
1.1	91.2	– 5.5	2.6•	100.0	+ 3.3			

•25 mg of Ca^{2+} was added as coprecipitant.

It is clear from Table 1 that thorium is quantitatively precipitated as the oxalate from homogeneous solution at a pH of 0.6-1.5; when the pH is increased, precipitation is incomplete. When a coprecipitant is present–calcium ions–thorium is quantitatively precipitated even at pH 2.62. Microcrystalloscopic examination of thorium oxalate obtained by the homogeneous precipitation method (Fig. 1), and that obtained by the normal oxalate method (Fig. 2), showed that in both cases the crystals are obtained in the form of rectangular tetragons, and sometimes in the form of rhombs; in the case of those obtained by homogeneous precipitation, however, the crystals fuse into each other and larger crystals are obtained with clearly defined edges.

Separation of thorium from zirconium, titanium and other elements. Separation of small amounts of thorium from foreign elements does not proceed quantitatively when the normal oxalate method is used. A method which has been adopted is to separate thorium beforehand as its insoluble fluoride [22, 30], this procedure also separates thorium from zirconium, titanium, niobium, tantalum, and some other elements. The use of fluorides in analysis is , however, undesirable–platinum vessels must be used, and the fluoride ion has to be carefully removed, etc. Tests were carried out on the separation of thorium from solutions containing zirconium, titanium, iron, the rare earths, and some other elements, using the homogeneous precipitation method; these were carried out as follows: to 100 ml of solution containing thorium, zirconium, titanium and the other elements indicated in Table 2 as their chlorides, at a pH of 3 (Congo red paper), was added 1 ml of a 25% solution of calcium chloride and 15 ml of acetonedioxalic acid solution. The solution was boiled for 15 minutes. On the next day the precipitate was filtered through a 9 cm diameter "blue band" filter paper and washed 3-4 times with a 1% solution of oxalic acid. The filter and precipitate were then dried in a 10 ml porcelain crucible, and finally ashed at 600-700°. The residue was transferred to a 50 ml beaker and moistened with



Thorium oxalate crystals obtained by ordinary (I), and homogeneous (II) precipitation.

water, it was then treated while being heated with 3-4 ml of concentrated hydrochloric acid. The acid having been removed so as to leave a damp salt, the residue was dissolved in 8-10 ml of water and transferred to a 25 ml standard flask. The solution was neutralized with ammonia to a pH of 3 (Congo red paper), 2 drops of hydrochloric acid sp.gr. 1.12 was added, and the volume made up to the mark with 0.09 N hydrochloric acid; thorium was finally determined by means of arsenazo [29]. Zirconium trapped by the precipitate of the oxalates of thorium, the rare earths, and calcium was determined by the alizarin method, while titanium was determined by means of hydrogen peroxide [31].

It is clear from Table 1 that thorium can be quantitatively separated from foreign ions by the homogeneous precipitation method. It should be noted that up to 50 γ zirconium and titanium are sometimes coprecipitated, i.e., they are coprecipitated in such amounts as would not interfere (in the presence of tartaric acid) with determination of thorium by means of arsenazo [29].

The rare earths, just like thorium, are precipitated, but they do not interfere in this determination.

A method for the determination of small amounts of thorium in natural materials. 0.5 g of dry sodium peroxide was placed in a 10 ml porcelain crucible and 5-6 mg of ferric oxide added, this was followed by 0.0250 – 0.2500 g of the test ore, and a further 2.5 – 4 g of sodium peroxide. This crucible was placed inside a similar crucible or inside a larger one and placed in a muffle where it was heated until a homogeneous melt (about 550°) was obtained. The cooled melt was dissolved in 60-100 ml of water by heating for 20-25 minutes. After 20 minutes the crucible was withdrawn from the beaker. The solution was filtered through a "white band" filter paper 9-11 cm in diameter, and the hydroxides on the paper washed 2-3 times with 0.5% sodium hydroxide, they were finally dissolved in 20-30 ml of hot 5% (by volume) hydrochloric acid. To this solution a saturated solution of sodium acetate was added until the pH was about 5 (reddening of Congo red paper), water was then added to bring the volume up to 100 ml; 1 ml of a 25% solution of calcium chloride and 15 ml of a

TABLE 2

Separation of Thorium from Foreign Elements

Taken					Found in the precipitate, in γ		
total rare earths, in mg	Zr^{4+} in mg	Ti^{4+} in mg	Fe^{3+} in mg	Th^{4+} in γ	Th^{4+}	Zr^{4+}	Ti^{4+}
10,0	10,0	6,0	-	38,68	35,0	20,0	—
10,0	10,0	6,0	—	38,68	37,5	—	—
10,0	10,0	6,0	—	38,68	37,5	10,0	—
10,0	10,0	6,0	300,0	38,68	37,5	40,0	5,0
10,0	10,0	6,0	300,0	38,68	35,0	—	—
10,0	10,0	6,0	300,0	38,66	37,5	—	—
10,0	10,0	6,0	300,0	38,63	37,5	—	5,0
10,0	10,0	6,0	300,0	38,68	32,5	50,0	—
0.5	5,5	4,0	60,0	112,0	110,0	50,0	—
0,5	5,5	4,0	60,0	112,0	112,0	10,0	—
0,5	5,5	4,0	60,0	112,0	110,0	—	—

TABLE 3

Determination of Thorium in Natural Materials

Sample number	Major components, in %	Thorium found, in %		Error (relative), in %
		by the fluoride-oxalate-thoron method	by the suggested method	
1	Total rare earths 0,5; ZrO_2 6,21 TiO_2 6,6; Fe_2O_3 62,1 Al_2O_3 11,92	0,12	0,11 0,12	— 2,8
2	Total rare earths 2,27; ZrO_2 7,32 Nb_2O_5 1,19	0,44	0,44 0,43	— 1,0
3	Total rare earths 2,10 ZrO_2 8,24 Nb_2O_5 1,08 Ta_2O_5 0,073	0,16	0,14 0,16 0,16 0,15.	— 5,0
4	Total rare earths 0,27 ZrO_2 9,9 Nb_2O_5 0,52 TiO_2 0,027	0,14	0,13 0,14 0,14	0,0
5	Total rare earths 2,24 ZrO_2 6,0 Nb_2O_5 0,47 TiO_2 1,58	0,17	0,15 0,16 0,17 0,17	— 5,0
6	$CaCO_3$	0,002	0,002 0,003	+12,5
7	—	0,005	0,004 0,005	—10,0
8	Total rare earths 2,27 ZrO_2 7,32	0,19	0,22 0,21	+13,0
9	—	0,006	0,005	—20,0
10	ZrO_2 70,0	1,51	1,52	+ 0,7
11	TiO_2 13,42	2,84	2,94	+ 3,6
12	—	0,0016	0,0016	0,00
13	—	0,002	0,002	0,00
14	—	0,040	0,033	—21,0
15	—	0,012	0,012	0,00
16	Total rare earths 0,48 ZrO_2 30,0 TiO_2 1,10 Fe_2O_3 3,80	0,44	0,40	—10,0
17	Total rare earths 0,24 ZrO_2 26,15 TiO_2 0,77 Fe_2O_3 6,60	0,22	0,20	—10,0

acetonedioxalic acid solution were finally added. The solution was boiled for 15-20 minutes and its volume made up to 100 ml again with water, when it was left to stand overnight. On the following day the solution was filtered through a 9 cm "blue band" filter paper. The residue was washed 4-6 times with a 1% solution of oxalic acid. The filter paper and residue were quantitatively transferred to a porcelain crucible in which they were dried and then calcined at 600-700°. This residue was, in turn, quantitatively transferred to a 50 ml beaker and a few drops of water and 4-5 ml of concentrated hydrochloric acid added. The mixture was evaporated until a moist residue was obtained, when another 3-4 ml of concentrated hydrochloric acid was added and the evaporation repeated until a moist residue was obtained again. This moist residue was dissolved in 8-10 ml of water and the solution obtained neutralized with ammonia until the pH was about 3 (Congo red paper); 2 drops of hydrochloric acid sp.gr. 1.12 was added to this solution and the whole transferred to a 25 ml standard flask, 0.5 ml of a 1% ascorbic acid solution was added and the volume made up to the mark with 0.09 N hydrochloric acid.

The solution was shaken up thoroughly and aliquots taken for thorium determination.

2-20 ml of the test solution was transferred to a 25 ml standard flask, and 0.5 ml of a 10% solution of tartaric acid, and 3 ml of a 0.05% solution of arsenazo added, the solution was made up to the mark with 0.09 N hydrochloric acid and thoroughly shaken up. The optical density was measured on a photocolorimeter in 30 mm cells at 570 mμ using a yellow-green filter.

When such a filter is not available it is necessary to combine a green filter with a liquid filter. A saturated solution of potassium dichromate placed in a 10 mm cell in the light path can be used as a liquid filter.

Calculations of the thorium content of the test material are then carried out on the basis of a calibration curve which had been constructed beforehand under the same conditions (from 5 γ to 70 γ of Th in 25 ml of solution).

It is clear from Table 3 that thorium can be determined with reasonable accuracy and reproducibility by the suggested method. Using this method it is possible to determine 0.002 – 3.0% of thorium in ores in the course of 10-12 hours, 10 samples being analyzed in this time.

SUMMARY

1. It has been established that precipitation of thorium from homogeneous solutions by means of acetonedioxalic acid has a number of advantages over the usual oxalate method: a coarse crystalline precipitate which is readily filtered is obtained, while zirconium and titanium are scarcely coprecipitated at all. Thorium can be precipitated quantitatively as the oxalate in the presence of foreign ions; precipitation can be carried out directly without any additional operations.

2. A new method has been developed for the determination of small amounts of thorium (0.002 – 3.0%) in natural materials, in which homogeneous precipitation is used in conjunction with the reagent arsenazo I.

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THE CHROMOMETRIC DETERMINATION OF SEXIVALENT MOLYBDENUM BY MEANS OF TUNGSTEN AND OTHER ELECTRODES*

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A number of papers have been published on the study of the potentiometric titration of sexivalent molybdenum with solutions of divalent chromium salts in media of HCl, H_2SO_4, etc. [1-14]. On the basis of the results obtained, chromometric methods of determining molybdenum in ferromolybdenum, molybdenum concentrates, and other materials have been developed. During titration of molybdenum and accompanying elements, the platinum indicator electrode was used.

On the titration curves obtained in dilute hydrochloric acid there are observed two potential jumps; the first jump—the larger one—corresponds to completion of the reduction of sexivalent molybdenum to the quinquevalent state, while the smaller jump corresponds to the completion of the reduction of the quinquevalent molybdenum to the trivalent state. In concentrated hydrochloric acid, the second jump is greater than the first. All previous investigators have not taken into account the fact that the second jump is located at such low potential values that the platinum electrode may partly function as a hydrogen electrode as a consequence of the acceleration on its surface of the reaction: $2Cr^{2+} + 2H^{+} = 2Cr^{3+} + H_2$. This should lead to a decrease in the second potential jump. Accordingly, it is of undoubted theoretical and practical interest to study the titration of sexivalent molybdenum with various electrodes made from materials on which there occurs a high hydrogen overvoltage (metallic mercury, graphite, tungsten, tantalum). It might be expected that such electrodes should permit one to obtain a more clearly defined potential jump for the final reduction of molybdenum to the trivalent state.

EXPERIMENTAL

Reagents, Apparatus and Titration Technique

A solution of sexivalent molybdenum was prepared by dissolving chemically pure ammonium molybdate in water.

This solution was standardized gravimetrically by the lead molybdate method [15]. The values thereby found were: 0.009606; 0.009590; 0.009570 on an average 0.009590 g/ml of Mo.

Solutions of the chloride and sulfate of divalent chromium were prepared and standardized by a method which has been described by one of the authors [16].

All titrations were carried out while a continuous stream of carbon dioxide was passed through the solutions, as is normally done in chromometric methods (without pre-reduction). The solutions being titrated were stirred by means of a mechanical stirrer.

The indicator electrodes used were the normal platinum electrode, a cup-shaped mercury electrode, an amalgamated platinum electrode, a tungsten electrode in the form of a rod (0.3 – 0.4 cm in diameter and 10 cm long) or a tungsten wire, a graphite electrode in the form of a rod (0.5 – 0.6 cm in diameter and 10 cm long),

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*From Li Kun's thesis (Moscow State University, 1958).

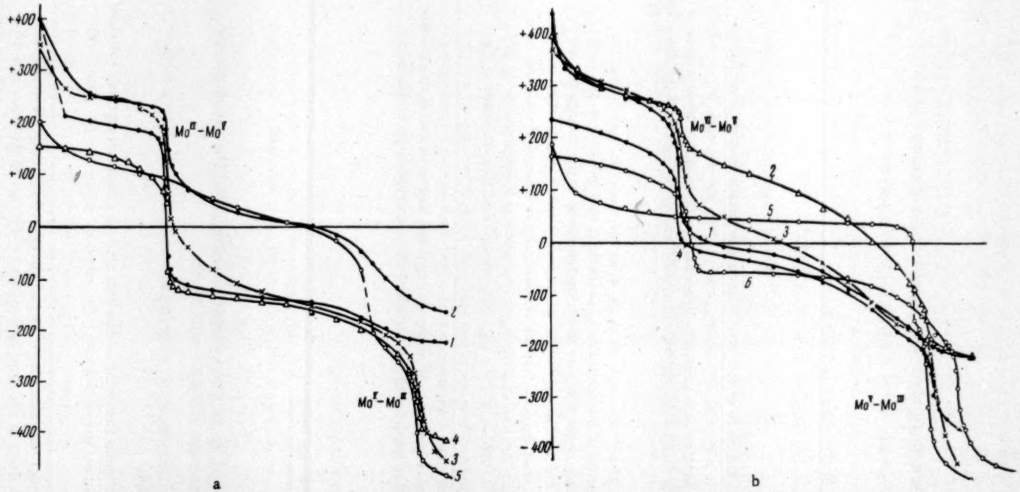

Fig. 1. Titration of sexivalent molybdenum with a divalent chromium salt solution in a sulfuric acid medium using various electrodes: $T_{Cr/Mo^{VI}-V}$ = = 0.009361; temperature 65-75°. Electrodes: 1) platinum; 2) amalgamated platinum; 2) graphite; 4) tungsten; 5) mercury; 6) tantalum.

a) 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) was taken. 70 ml of 10% H_2SO_4 was added. The first potential jump ($Mo^{VI} \rightarrow Mo^{V}$) for the platinum, amalgamated platinum, graphite and tungsten electrodes was observed on adding 5.20 ml of $CrCl_2$ solution. This corresponds to 0.04868 g Mo. The first potential jump was not observed in the case of the mercury electrode. The second potential jump occurred($Mo^{V} \rightarrow Mo^{III}$) on addition of 15.40 ml of $CrCl_2$ solution (0.04805 g Mo) in the case of the tungsten and graphite electrodes, on addition of 15.30 ml $CrCl_2$(0.04777 g Mo) in the case of the mercury electrode; no jump was observed in the case of the platinum electrode.

b) 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) was taken. 70 ml of 30% sulfuric acid was added. The first potential jump($Mo^{VI} \rightarrow Mo^{V}$) for the platinum, amalgamated platinum, graphite, and tungsten electrodes was observed on adding 5.20, 5.30, 5.20, and 5.20 ml respectively of $CrCl_2$ (0.04868, 0.04961, 0.04868, and 0.04961 g of Mo). The mercury electrode did not give a potential jump. The second potential jump ($Mo^{V} \rightarrow Mo^{III}$) occurred for the amalgamated platinum, graphite, tungsten, and mercury electrodes on addition of 15.30, 15.50, 15.50, and 15.30 ml of $CrCl_2$ solution respectively (0.04777, 0.04836, 0.04777 g Mo). The second potential jump was not given by the platinum electrode.

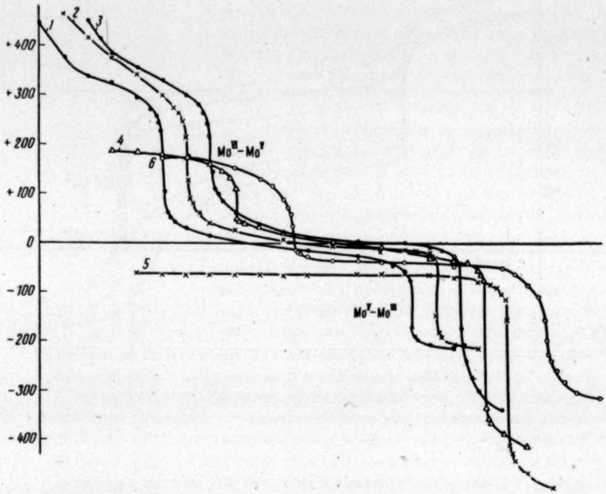

Fig. 2. Titration of sexivalent molybdenum in hydrochloric acid when various indicator electrodes are used.
5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) was taken; 70 ml of HCl 1 : 1 was used; temperature 70-75°;

$$T_{Cr/Mo^{VI} \rightarrow V} = 0.009490$$

Electrodes: 1) platinum; 2) amalgamated platinum; 3) graphite; 4) tungsten; 5) mercury; 6) tantalum. The first potential jump ($Mo^{VI} \rightarrow Mo^{V}$) on the platinum, amalgamated platinum, graphite, and tungsten electrodes was found on addition of 5.10 ml of $CrCl_2$ solution (0.04840 g). The first jump was not observed with a mercury electrode. The second jump ($Mo^{V} \rightarrow Mo^{III}$) was found after addition of 15.30 ml of $CrCl_2$ solution (0.04840 g Mo) for all the electrodes studied.

and a tantalum electrode in the form of a plate. The reference electrode was a saturated calomel electrode (all potentials are given with reference to this electrode).

Titration was carried out by a compensation method (P-4 potentiometer) in hydrochloric acid (10 or 30%) at 65-75°, or in a sulfuric acid medium. For each titration 5.0 ml of 0.1 M ammonium molybdate (0.009590 g/liter Mo) was taken together with 70 ml of 10 or 30% hydrochloric acid or 70 ml of 18% sulfuric acid. The beaker used for titration had a capacity of 150 ml. Near the equivalence point the solution of divalent chromium salt was added in 0.10 ml aliquots.

Titration curves obtained in a sulfuric acid medium are shown in Fig. 1a and b, while those obtained in hydrochloric acid are shown in Fig. 2.

DISCUSSION OF RESULTS

It is clear from Fig. 1a and b that the second potential jump obtained during titration of molybdenum in a sulfuric acid medium increases sharply on replacing the platinum electrode by a tungsten and by a graphite electrode, as was to be expected. During titration with a mercury electrode there is observed one large potential jump corresponding to completion of the reduction of molybdenum to the trivalent state. In addition, when

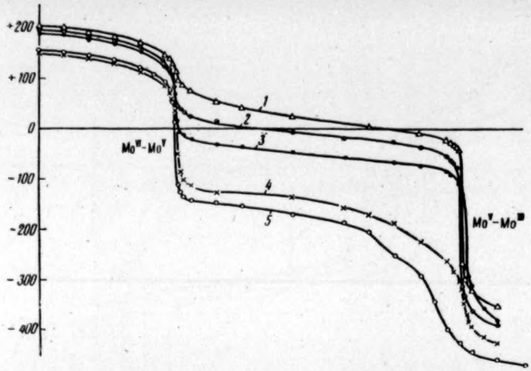

Fig. 3. Effect of sulfuric or hydrochloric acid concentration on the titration curves of sexivalent molybdenum when a tungsten electrode is used. 5.0 ml lots of 0.1 M ammonium molybdate (0.04795 g Mo) taken together with 70 ml of H_2SO_4 or HCl of varying concentrations; temperature 65-70°; $N_{CrCl_2} = 0.09091$; $T_{Cr/Mo} = 0.008723$. Curve 1) 70 ml HCl 2 : 1; 2) 70 ml HCl 1 : 1; 3) 70 ml HCl 1 : 2; 4) 70 ml 10% H_2SO_4; 5) 70 ml 4% H_2SO_4. The first potential jump on curves 1-5 was observed on addition of 5.50 ml of $CrCl_2$ solution (0.04797 g Mo). The second potential jump found on Curves 1 and 2 was on addition of 16.60 ml of $CrCl_2$ (0.04827 g Mo); on Curve 3 the jump was observed after addition of 16.80 ml of $CrCl_2$ solution (0.04885 g Mo); on Curve 4, on addition of 16.70 ml of $CrCl_2$ (0.04856 g Mo); on Curve 5 no potential jump was observed.

a mercury electrode is used, another jump can be observed before the molybdenum changes over into the trivalent state (the dotted line on Curve 5 Fig. 1a and b). The position of this jump changes from titration to titration and is connected with the disappearance of the film formed earlier on the mercury surface. A potential jump corresponding to completion of the reduction of sexivalent to quinquevalent molybdenum is not observed. This can be explained by the fact that mercury in a strongly acid medium reduces a small amount of sexivalent molybdenum to the quinquevalent state with formation of an equivalent amount of univalent mercury ions (formation of a film can be observed on the mercury surface). The reaction proceeds on the electrode surface. During titration with a solution of a divalent chromium salt there occurs reduction of both molybdenum and of the ions of univalent mercury formed (the film on the mercury surface dissolves), accordingly, there is observed a potential jump at the point corresponding to completion of reduction of molybdenum to the trivalent state. Obviously, a mercury indicator electrode can only be used during titration of sexivalent molybdenum in pure solutions, and in the presence of elements which are not reduced by divalent chromium ions. This fact appreciably lowers the practical value of the mercury indicator electrode. As for the amalgamated platinum electrode, this functions approximately like a platinum electrode and not like a mercury electrode. When an amalgamated platinum electrode is used there is observed a comparatively small but quite clearly defined potential jump on completion of the reduction of sexivalent molybdenum to the quinquevalent state, while with a platinum electrode (under equal conditions) there is observed a well defined potential jump. When a platinum electrode and an amalgamated platinum electrode are used respectively, a clearly defined potential jump is not observed at the point corresponding to completion of reduction of quinquevalent molybdenum to the trivalent state under the conditions chosen.• With a tantalum electrode there are observed two clearly defined

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•An amalgamated platinum electrode behaves like a platinum electrode not only during titration of sexivalent molybdenum, but also during titration of quadrivalent titanium with a solution of a divalent chromium salt [17].

potential jumps corresponding to completion of the reudction of sexivalent molybdenum to the quinquevalent state, and completion of the reduction of quinquevalent molybdenum to the trivalent state, in that order. This electrode, however, has no advantages over the tungsten or graphite electrodes for carrying out potentiometric titrations.

It should be noted that during titration of molybdenum in sulfuric acid, tne potential of all the electrodes studied, during the transition from Mo^{V} to Mo^{III} is not established rapidly; accordingly, near tne end-point it is necessary to wait for 2-3 minutes after addition of each aliquot of the divalent chromium salt solution.

It is clear from Fig. 2 that during titration of sexivalent molybdenum in a hydrochloric acid medium, when various indicator electrodes were used, in general, the same features are observed as for titration in a sulfuric acid medium. The essential difference is that with a platinum and with an amalgamated platinum electrode in a hydrochloric acid medium there is observed a completely clearly defined second potential jump, while when sulfuric acid is used this second jump is not observed when the electrodes indicated are used. The second potential jump is very distinct when tungsten and graphite electrodes are used, and, when identical conditions are used, this jump is approximately twice the jump obtained with a platinum indicator electrode, and extends into a region of considerably more negative potentials.

The potential of the platinum, amalgamated platinum, graphite, and tantalum electrodes in a medium of HCl 1 : 1 is established slowly during reduction of Mo^{VI} to Mo^{V} and of Mo^{V} to Mo^{III}. The potential of the tungsten and mercury electrodes is established rapidly.

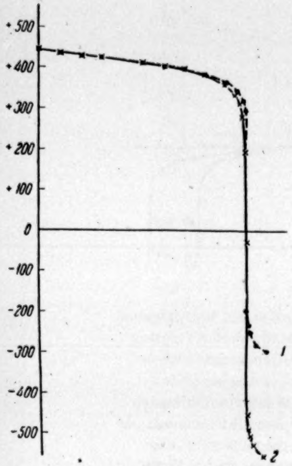

Fig. 4. Titration of trivalent ion with $CrCl_2$ using tungsten and platinum indicator electrodes.
Solutions taken: 10.0 ml 0.1000 N $K_2Cr_2O_7$, 0.6 g Mohr salt, and 40 ml 4% H_2SO_4; room temperature; N_{CrCl_2} = = 0.09980. The equivalence point in both cases was found on addition of 10.2 ml of $CrCl_2$; 1) platinum electrode; 2) tungsten electrode.

Thus, the tungsten indicator, and also the graphite indicator electrodes have undoubted advantages over the platinum electrode during titration of sexivalent molybdenum in a medium both of sulfuric acid and of hydrochloric acid. The distinct and fairly large potential jump observed at the second equivalence point ensures the accurate establishment of the titration end-point, even for small amounts of molybdenum; this leads to an increase in the reliability and accuracy of molybdenum determination, including molybdenum determinations carried out in the presence of other elements.

The effect of the concentration of hydrochloric or sulfuric acid on the titration curves of sexivalent molybdenum when a tungsten indicator electrode is used, is shown in Fig. 3.

On completion of the reduction of sexivalent molybdenum to the quinquevalent state in a hydrochloric acid medium (2 : 1, 1 : 1, and 1 : 2) there are observed comparatively small, but still quite distinct, potential jumps on the tungsten electrode. The first potential jumps increase with decreasing hydrochloric acid concentration. During titration in a hydrochloric acid medium, the second potential jumps which correspond to completion of reduction of quinquevalent molybdenum to the trivalent state, are considerably larger than the first. The value of the potential jumps increase, in this case, with increasing hydrochloric acid concentration.

Up to the first potential jump, the potential of the tungsten electrode is established rapidly in HCl. Between the first and second jumps, the potential is established rapidly in HCl (2 : 1) and (1 : 1), but slowly in HCl (1 : 2).

When sulfuric acid is used (10 and 4%), large and distinct potential jumps are observed for the tungsten electrode on completion of the reduction of sexivalent molybdenum to the quinquevalent state. With increasing sulfuric acid concentration, the potential jump increases somewhat.

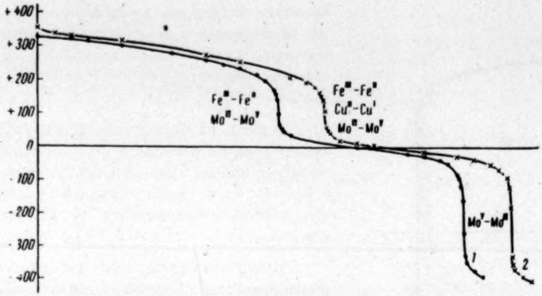

Fig. 5. Titration curves obtained for a solution of sexivalent molybdenum, trivalent iron, and divalent copper in hydrochloric acid, when a tungsten electrode is used. Capacity of titrating cell 250 ml; temperature 65-70°; N_{CrCl_2} = 0.09090; $T_{Cr/Mo}$ = 0.008723.
Curve 1) 5.0 ml of 0.2 M $NH_4Fe(SO_4)_2$, 5.0 ml 0.1 M ammonium molybdate (0.04795 g Mo) and 70 ml HCl 1 : 1. The first potential jump was observed on addition of 14.30 ml of $CrCl_2$ solution, while the second jump was observed after addition of 25.40 ml of $CrCl_2$ solution. Curve 2) 5.0 ml of 0.2 M $NH_4Fe(SO_4)_2$, 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo), 2.0 ml of 0.1 N $CuSO_4$, 70 ml HCl 2 : 1. The first potential jump was observed after addition of 17.2 ml of $CrCl_2$ solution, while the second jump was observed after addition of 28.30 ml of $CrCl_2$ solution. In both cases 11.10 ml of $CrCl_2$ (0.04841 g Mo) was used up in reducing quinquevalent molybdenum to the trivalent state.

The potential jump corresponding to reduction of quinquevalent molybdenum to the trivalent state in a medium of 10% sulfuric acid is less distinct than the first jump; it is located at very low potentials, but it is still completely suitable for use in potentiometric titration.

In 4% sulfuric acid the second potential jump is comparatively poorly defined. Molybdenum should be titrated in sulfuric acid by means of the second potential jump only in those cases, where for some reason or other, it is not expedient to work in hydrochloric acid.

On the basis of the results obtained the following conclusions can be drawn. When sulfuric acid is used, molybdenum should be titrated by means of the first potential jump given by a tungsten electrode, while when hydrochloric acid is used with the same indicator electrode, the second potential jump is the best to use, although in this case the first jump could also be used. The dissimilar behavior of molybdenum during titration in sulfuric and hydrochloric acid presumably can be explained by the difference in the state of the molybdenum ions in the sexi-, quinque- and trivalent state in such solutions (in particular, by formation of complex ions). This point will be the subject of a special investigation.

Potentiometric Determination of Molybdenum in Ferromolybdenum Using a Tungsten Electrode

It is necessary to determine molybdenum sometimes in technical materials in the presence of iron and other elements which are also reduced by divalent chromium ions. We accordingly undertook a study of the titration of accompanying elements using a tungsten electrode, and also studied the possibility of titrating molybdenum and other elements in succession.

As is evident from Fig. 4, during titration of iron in a medium of hydrochloric acid with $CrCl_2$ using a tungsten indicator electrode, there is observed a large potential jump at the equivalence point. The potential jump is located on the same place on the titration curve when a tungsten electrode is used as when a platinum

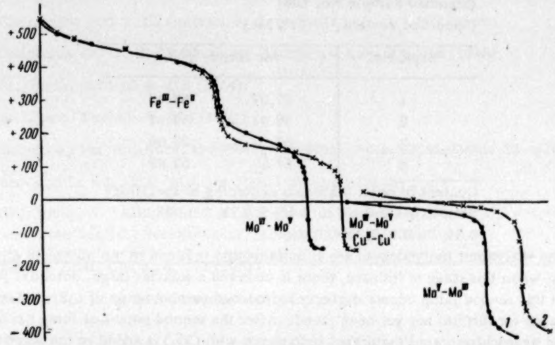

Fig. 6. Separate determination of iron and molybdenum in the absence and in the presence of copper when a tungsten electrode is used. Capacity of titration cell 250 ml; N_{CrCl_2} = 0.09560; $T_{Cr/Mo}$ = 0.009174. Curve 1) 5.0 ml of 0.2 M $(NH_4)_2Fe(SO_4)_2$, 5.0 ml 0.1 M ammonium molybdate (0.04795 g Mo) and 40 ml of 4% H_2SO_4 taken. The first potential jump ($Fe^{III} \rightarrow Fe^{II}$) occurred on addition of 10.40 ml of $CrCl_2$ solution, the second jump ($Mo^{VI} \rightarrow Mo^{V}$) was observed on addition of 15.70 ml of $CrCl_2$. After addition of concentrated hydrochloric acid (100 ml) and titration continued, the third jump ($Mo^{V} \rightarrow Mo^{III}$) was observed after addition of 26.30 ml of $CrCl_2$. 0.04862 g of Mo was found. Curve 2) 5.0 ml of 0.2 M $NH_4Fe(SO_4)_2$, 5.0 ml of 0.1 M molybdate (0.04795 g Mo), 2 ml of 0.1 N $CuSO_4$, and 40 ml of 4% H_2SO_4 were taken. The first potential jump ($Fe^{III} \rightarrow Fe^{II}$) occurred on addition of 10.2 ml of $CrCl_2$, the second jump ($Mo^{VI} \rightarrow Mo^{V}$ and $Cu^{II} \rightarrow Cu^{I}$) was observed after addition of 17.80 ml of $CrCl_2$. After this, 100 ml of concentrated hydrochloric acid was added; the solution was heated to 60-70° and titration continued. The third jump ($Mo^{V} \rightarrow Mo^{III}$) was observed on addition of 28.40 ml of $CrCl_2$. Thus, 10.6 ml of $CrCl_2$ was used up for the reduction of Mo^{V} (Mo found = 0.04862 g).

electrode is used. Thus, the tungsten electrode is fully suitable instead of the platinum indicator electrode for the titration of trivalent iron in dilute sulfuric acid. Near the equivalence point it is necessary to titrate slowly, time being given for the potential to be established after addition of each fresh aliquot of $CrCl_2$ solution. On the titration curve obtained for a mixture of sexivalent molybdenum, trivalent iron, and divalent copper in a hydrochloric acid medium. (2 : 1), when the tungsten indicator electrode is used (Fig. 5), the first potential jump, which is small but quite distinct, is observed on completion of the simultaneous reduction of the elements indicated to the quinquevalent, divalent, and univalent states respectively; the second, very large jump, corresponds to the completion of the reduction of quinquevalent molybdenum to the trivalent state. Subsequently, univalent copper is reduced to the metal. The amount of chromous chloride used between the first and second potential jumps corresponds to the amount of molybdenum present. Completely satisfactory results have been obtained for molybdenum. Thus, by using a hydrochloric acid medium, it is possible to determine molybdenum in the presence of trivalent iron and divalent copper by means of a tungsten indicator electrode. The amounts of iron and copper, however, cannot be determined at the same time.

Separate determination of iron and molybdenum in the presence, and in the absence of copper is possible under the following conditions (using a tungsten indicator electrode) (Fig. 6). Titration is carried out initially in a CO_2 atmosphere in 4.0% sulfuric acid (40 ml) at room temperature. Under such conditions trivalent iron is first reduced; when this stage is complete there is observed a small but quite distinct potential jump. After this,

Determination of Molybdenum in Ferromolybdenum
(Standard Sample No. 168)
(Specified content, 57.01% Mo)

Expt. No.	Mo found, in %	
1	57.07	57.48
2	56.94	57.07
3	57.12	56.98
4	57.30	57.09

Content of other materials according to specification, in % Cu 0.15; Si 0.55; S 0.23; P 0.032; Cu 0.39; Sn 0.016; Sb 0.018.

divalent copper and sexivalent molybdenum are simultaneously reduced to the univalent and quinquevalent states respectively; when this stage is finished, there is observed a second, large, potential jump. Nevertheless the point at which this second jump occurs is poorly reproduced (over a range of 0.2 – 0.3 ml of 0.1 N $CrCl_2$ solution). The reason for this has not yet been found. After the second potential jump has been reached, 100 ml of concentrated hydrochloric acid (saturated beforehand with CO_2) is added to the solution being titrated, and the whole heated to 60-70°; titration is then continued until a third potential jump is obtained which corresponds to completion of reduction of quinquevalent molybdenum to the trivalent state. The volume of $CrCl_2$ solution expended between the second and third jumps corresponds to the amount of molybdenum present.

When reduction of molybdenum to the trivalent state is complete, reduction of univalent copper to the metal occurs. Satisfactory results have been obtained for iron and molybdenum; the results for copper were poor.

Potentiometric determination of molybdenum in ferromolybdenum is carried out as follows.

One g of finely ground ferromolybdenum is dissolved in a 300 ml beaker in a mixture of 20 ml HNO_3 (1 : 1) and 20 ml H_2SO_4 (1 : 1), and the solution evaporated until the appearance of white fumes of H_2SO_4. After cooling, 70-80 ml of water is added and the mixture heated until the salts dissolve. The cooled solution plus undissolved silica is transferred to a 250 ml standard flask; 100 ml of water is added and the whole shaken thoroughly—this is essential in order to get a homogeneous solution; the volume is then made up to the mark with water. Twenty-five ml of this solution is pipetted into a 250 ml beaker which is to be used for titration, 70 ml of HCl (2 : 1) is then added and the solution heated; CO_2 is passed through the solution to be titrated for 30 minutes, and the solution then titrated slowly with 0.1 N $CrCl_2$ solution at 70°. The indicator electrode used is a tungsten wire. Titration is carried out until a second potential jump is obtained, the chromous chloride used up between the first and second jumps corresponds, as indicated above, to the molybdenum content.

Results obtained by this method are given in the Table.

SUMMARY

A study has been made of the titration of sexivalent molybdenum in hydrochloric and sulfuric acid media, using a divalent chromium salt as titrant, and using various indicator electrodes. A chromometric method has been developed for the determination of molybdenum in ferromolybdenum using a tungsten indicator electrode.

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THE COPRECIPITATION OF ZINC WITH COMPLEX COMPOUNDS CONTAINING PYRIDINE

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The capacity of zinc to be coprecipitated with precipitates of $[MePy_2]X_2$ (where Me is Cu^{2+}, Cd^{2+}, Ni^{2+} and X is SCN^- or Br^-) has already been noted; at that time we very briefly indicated that there is a direct relation between the amounts of the macro- and micro components in solution before precipitation, and the amount of precipitated microcomponent [1]. Such a relation was found in the case of the coprecipitation of cadmium during precipitation of mercury with antipyrine and bromide [2]. We have studied this relation further together with other questions in more detail. Results of these studies are described in the present article.

We shall first of all deal with copreipitation of zinc with $[CuPy_2](SCN)_2$.

Experiments were carried out as follows. In the first series of experiments 1 ml of a 1% solution of ammonium thiocyanate and 0.5 ml of a 10% solution of pyridine were added to 1.5 ml of a solution which was 0.25 N nitric acid, and contained 50 γ of Zn^{2+} and variable amounts of Cu^{2+}. Preliminary tests showed that zinc, when taken separately, does not form a precipitate under the conditions used, but can be precipitated as a result of coprecipitation. The precipitate of $[CuPy_2](SCN)_2$ was washed with a 1% solution of pyridine, and then dissolved in the least possible volume of 1 N nitric acid, and finally titrated from a microburet with 0.1 N silver nitrate in the presence of ferric alum. On the basis of these results the weight of the precipitate was calculated. One ml of 0.1 N silver nitrate corresponds to 16.9 mg of $[CuPy_2](SCN)_2$. After addition of ammonia to the solution obtained, the amount of coprecipitated zinc was determined radiometrically. For this purpose some of the radioactive isotope Zn^{65} was added to the solution used for the work. The specific activity was within the limits of 60-80 impulses/minute per γ of zinc.

The second series of experiments was carried out under the same conditions, but, in this case, the amount of copper was kept constant, while the amount of zinc was altered. 3-5 experiments were carried out in parallel for the given amount of components; usually, they gave almost identical results. On the basis of the results obtained the amount of zinc in 1 mg of the precipitate was calculated, as well as the ratio of the amounts of copper and zinc in the precipitate. When these calculations were made, it was borne in mind that 1 mg of $[CuPy_2](SCN)_2$ contained 189 γ copper.

From the results of the two series of experiments which were carried out at 15-17° (Table 1), it is clear that, if, before precipitation, the amount of copper in solution was, for example, 10 times the amount of zinc, then the amount of copper in the precipitate obtained from this solution was 85 times the amount of zinc. Thus, the relative zinc content of the precipitate is 8.6 times less than in the original solution. This ratio was found to be almost constant in all experiments (Table 1) and equal to 6-8. The small variations around these values can be explained by experimental errors.

It also follows from Table 1 that with increasing copper content of the original solution, or with decreasing amounts of zinc, the content of the latter in the precipitate increases in the first case, and decreases in the second. Nevertheless, in both cases, the amount of coprecipitated zinc found in unit weight of precipitate decreases, and this decrease, as is evident from Fig. 1, is a function of the ratio of $Cu^{2+} : Zn^{2+}$ in the solution before precipitation.

TABLE 1

Coprecipitation of Zinc with $[CuPy_2](SCN)_2$

Contents of solution components before precipitation, in γ		Weight of precipitate, in g		Zinc coprecipitated		Ratio in parts by weight of:	
Zn^{2+}	Cu^{2+}	calc.	found	in γ	in γ/mg of precipitate	in solu. before precip.	in the precipitate
50	500	2,7	2,9	6,3	2,2	10	86
50	750	4,0	4,3	6,5	1,5	15	126
50	1000	5,3	5,8	6,6	1,1	20	172
50	1500	8,0	8,4	6,7	0,8	30	236
50	2000	10,6	10,9	7,0	0,6	40	315
40	1000	5,3	5,8	5,2	0,9	25	210
30	1000	5,3	5,6	4,2	0,7	33	270
20	1000	5,3	5,8	3,2	0,55	50	343
10	1000	5,3	5,4	1,9	0,33	100	572

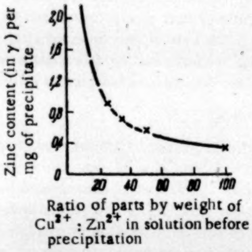

Fig. 1. Zinc content of the precipitate of $[CuPy_2](SCN)_2$ as a function of the ratio in parts by weight of copper and zinc in the solution before precipitation.
–) Experiments carried out with a constant amount of zinc; x) experiments carried out with a constant amount of copper.

The results obtained during the first and second series of experiments lie quite well on one curve. This relation is even more clearly demonstrated in Fig. 2 (Curve 3). The linear nature of this relationship makes it possible to forecast the extent of coprecipitation of zinc under the conditions indicated for the precipitation of $[CuPy_2](SCN)_2$, as long as the contents of the components in the original solution are known.

Similar characteristics were observed during the coprecipitation of zinc with $[CdPy_2](SCN)_2$ and $[NiPy]_2(SCN)_2$.

For precipitating the cadmium compound, 0.25 ml of a 1% solution of ammonium thiocyanate and 0.25 ml of a 10% solution of pyridine were added to 2.5 ml of a solution of a cadmium salt. Since the solubility of $[CdPy_2](SCN)_2$ in water is appreciable, we carried out these tests at 0°. The conditions used for precipitating nickel were the same as those used for copper. Precipitation was carried out at 18-20°. During calculation, it was borne in mind that 1 mg of $[CdPy_2](SCN)_2$ contains 290 γ of cadmium, while 1 mg of $[NiPy_2](SCN)_2$ contains 176 γ of nickel.

The results of these experiments are given in Tables 2 and 3.

In both cases the relative amount of zinc in the precipitate was approximately 1.5 times less than in the original solution. This value was reproduced fairly well in all the experiments; a linear relation was found between the ratio of the amounts of the components in the solution before precipitation, and the amount of coprecipitated zinc contained in unit weight of the precipitate. These results are illustrated in Fig. 2 (Curves 1 and 2).

A series of experiments was carried out on the coprecipitation of zinc with $[CdPy_2]Br_2$.

One ml of a solution containing cadmium and zinc salts was mixed at 18-20° with 0.25 ml of a 50% solution of potassium bromide and 0.25 ml of a 10% pyridine solution. The precipitate formed was washed with 1% pyridine solution, after which it was dissolved in 0.2 ml of 0.1 N nitric acid; the amount of coprecipitated zinc in the solution obtained was determined radiometrically (Table 4). For purposes of calculation it was taken into account that 1 mg of this precipitate contained 263 γ of cadmium.

In the case under consideration, coprecipitation was less, and, consequently, the precipitate contained less zinc than in all the previous cases. Nevertheless, a constant ratio between the components in solution before precipitation and in the precipitate was not observed here; the decrease in the relative amount of zinc in the

TABLE 2

Coprecipitation of Zinc with $[CdPy_2](SCN)_2$

Contents of solution components before precipitation, in γ		Weight of precipitate, in g		Zinc coprecipitated		Ratio in parts by weight of:	
Cd^{2+}	Zn^{2+}	calc.	found	in γ	in γ/mg of precipitate	in solu. before precip.	in the precipitate
300	50	1,03	1,12	34,2	30,5	6	9
500	50	1,72	1,86	34,1	18,3	10	15
750	50	2,52	2,74	33,5	12,2	15	23
1000	50	3,44	3,67	32,8	8,9	20	32
1000	40	3,44	3,67	24,5	6,6	25	44
1000	25	3,44	3,67	14,7	4.0	40	72
1000	12,5	3,44	3,67	6,8	1,8	80	161

TABLE 3

Coprecipitation of Zinc with $[NiPy_2](SCN)_2$ (weight of precipitate 5.7 mg)

Contents of solution components before precipitation, in γ		Zinc coprecipitated		Ratio in parts by wt. of: $Ni^{2+} : Zn^{2+}$	
Ni^{2+}	Zn^{2+}	in γ	in γ/ mg of precipitate	in solu. before precip.	in the precipitate
1000	50	36,0	6,3	20	27
1000	40	27,6	4,8	25	36
1000	30	20,7	3,6	33	48
1000	20	13,8	2,3	50	76
1000	10	6,9	1,2	100	100

TABLE 4

Coprecipitation of Zinc with $[CdPy_2]Br_2$

Contents of solution components before precipitation, in γ		Weight of precipitate, in g		Zinc coprecipitated		Ratio in parts by weight of:	
Cd^{2+}	Zn^{2+}	calc.	found	in γ	in γ/mg of precipitate	in solu. before precip.	in the precipitate
1000	50	3,8	3,7	0,3	0,081	20	3209
1500	50	5,7	5,6	0,4	0,071	30	3662
2000	50	7,6	7,3	0,4	0,055	40	4727
2500	50	9,5	9,2	0,5	0,054	50	4814
5000	50	19,0	18,6	0,6	0,032	100	8109
2000	40	7,6	7,3	0,25	0,034	50	7647
2000	30	7,6	7,3	0,15	0,020	66	13000
2000	20	7,6	7,3	0,1	0,013	100	26000

precipitate varied from 80-200 times. These variations can be explained on the basis of the small extent of coprecipitation, as a result of which the accuracy of determination of coprecipitated zinc is not high. All the same, even in these experiments, there is still observed the same qualitative relationship as in all the reactions noted above (Fig. 2, Curve 4). In all cases there is observed a quite definite relation between the ratio of the

TABLE 5

Coprecipitation of Zinc with $[CuPy_2](SCN)_2$ as a Function of the Temperature (1000 γ Cu^{2+} and 50 γ Zn^{2+}; theoretical weight of precipitate 5.3 mg)

Temp. in °C	Wt. of precipitate, mg	Zinc coprecipitated	
		in γ	in γ/mg of precipitate
0	5,2	7,8	1,5
10	5,2	7,0	1,3
20	5,2	6,0	1,1
30	5,2	3,5	0,7
40	5,1	2,8	0,55
60	5,2	2,0	0,4
80	5,1	1,0	0,2
100	5,1	0,4	0,08

TABLE 6

Coprecipitation of Zinc with $[CuPy_2](SCN)_2$ at 100° as a Function of the Amount of Zinc in Solution (1000 γ Cu^{2+}; theoretical weight of precipitate 5.3 mg)

Zinc content, in γ	Wt. of precipitate, mg	Zinc coprecipitated	
		in γ	in γ/mg of precipitate
100	5,1	0,48	0,09
150	5,1	0,84	0,16
200	5,1	1,90	0,37
500	5,3	101,0	19,0
750	5,6	254,0	45,3
1000	6,0	462,0	77,0

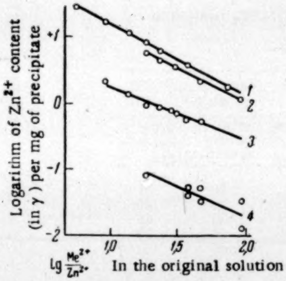

Fig. 2. Relationship between the ratio of the amounts of the components in the solution before precipitation, and the zinc content of 1 mg of precipitate (on a logarithmic scale):

1) precipitation of $[CdPy_2](SCN)_2$;
2) precipitation of $[NiPy_2](SCN)_2$;
3) precipitation of $[CuPy_2](SCN)_2$;
4) precipitation of $[CdPy_2]Br_2$.

amounts of the components in the original solution, and in the precipitate obtained from this solution. (Fig. 2). A significant fact is that all the lines in Fig. 2 are almost parallel to each other. This indicates the general nature of the relationship observed (at least in the case of the reactions studied). That such relationships are possible, can probably be attributed to the fact that in each series of experiments, when the temperature is kept constant, the relative amount of coprecipitated zinc (as a percentage) is almost a constant.

Experiments showed that the extent of the coprecipitation of zinc with $[CuPy_2](SCN)_2$ and $[CdPy_2]Br_2$ is small. By using these reactions it is possible to carry out a fairly satisfactory separation of zinc from copper or cadmium. Microdetermination of the last two cations as the complex compounds indicated gives completely satisfactory results, since the weight of precipitate determined experimentally coincides with the theoretical value within the limits of experimental error (Tables 1 and 4). Separation of copper and zinc can be carried out with even greater completeness, by precipitating $[CuPy_2](SCN)_2$ at an elevated temperature (Tables 5 and 6).

On increasing the temperature of a solution containing 1000 γ Cu^{2+} and 50 γ Zn^{2+} to 100°, the weight of precipitate obtained hardly changes at all, but the amount of zinc which is coprecipitated decreases sharply. On increasing the amount of zinc in the solution while the copper content is kept constant, the weight of the precipitate gradually increases, and the quantity of zinc coprecipitated also increases.

It is of interest to note that in an experiment in which 500 γ of Zn^{2+} was used, the theoretical amount of precipitate was obtained, this apparent high accuracy is, of course, the result of mutual compensation of counteracting sources of error; incomplete precipitation of copper is compensated by coprecipitation of zinc. These results show that 200 γ of Zn^{2+} can be satisfactorily separated from 1000 γ copper, and that quantitative microdetermination of copper by precipitation of the compounds indicated [3] gives satisfactory results, even when small amounts of zinc are present in the solution. Furthermore, the results indicated above for the theoretical weight of precipitate, and that found by titration, show that a titrimetric method is fully applicable

TABLE 7

Titrimetric Microdetermination of Copper in the Presence of Zinc

Content in γ of:		0.1 N $AgNO_3$ used, in ml	Cu^{2+} found, in γ	Error	
Cu^{2+}	Z^{2+}			in γ	in %
1000	50*	0,30	953	47	4,7
1000	100*	0,30	953	47	4,7
1000	150*	0,30	953	47	4,7
1000	200*	0,30	953	47	4,7
1000	500*	0,32	1017	17	1,7
1000	750*	0,33	1048	48	4,8
1000	1000*	0,35	1112	112	11,2
1000	10**	0,32	1017	17	1,7
1000	20**	0,34	1080	80	8,0
1000	30**	0,33	1048	48	4,8
1000	40**	0,34	1080	80	8,0
1000	50**	0,34	1080	80	8,0

*Precipitation at 100°.

**Precipitation at 20°.

to the determination of copper in the form of $[CuPy_2](SCN)_2$. Naturally, a titrimetric microdetermination can be carried out appreciably more rapidly and simply than a gravimetric determination. Table 7 contains results obtained during the titrimetric microdetermination of copper in the presence of zinc. Precipitation of $[CuPy_2](SCN)_2$ was carried out at room temperature and at 100° from 3 ml of a nitric acid solution. Precipitation conditions, as well as washing and titrating were the same as those described above.

SUMMARY

It has been found that during the coprecipitation of zinc with $[MePy_2](SCN)_2$ there exists a definite relationship between the amounts of the components in solution before precipitation and in the precipitate formed.

The amount of zinc which is coprecipitated decreases sharply with increasing temperature; this makes it possible to separate copper from zinc, and to determine copper quantitatively in solution.

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A STUDY OF THE REACTION OF CUPRIC IONS WITH POTASSIUM THIOCYANATE

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It is known that black cupric thiocyanate $Cu(SCN)_2$ is gradually reduced to CuSCN in aqueous media [1]. When the solution is diluted with water CuSCN is deposited in the form of a white precipitate. Philip and Bramley [1] were of the opinion that in acetone solution the reduction proceeds considerably more slowly than in water. Reduction occurs readily in the presence of any reducing agent, for example sulfurous acid. A number of research workers have used this reaction for the quantitative determination of copper [2-5]. Kul'berg and Gorlinskii [6] have studied the interaction of cupric ions with potassium thiocyanate taken in excess, by means of a spectrophotometric method in aqueous acetone solution; they concluded that the reason for the color is the formation of cuprothiocyanate ions $[Cu(SCN)_n]^{n-2}$, where n is 3 or 4. Later, Kitson [7], and Oudinet and Gallais [8], carried out some work with the aim of establishing an accurate formula for cuprothiocyanate complexes, and for determining the stability of these complexes in 50% and 70% acetone-water mixtures; they carried out this work on an electrophotometer. These authors, using Job's method [9], determined the composition and instability constants of the thiocyanate complexes of divalent copper in aqueous acetone solutions; they found that, depending on the concentration of the alkali metal thiocyanate, several complexes can exist at the same time: $[Cu(SCN)_3]^-$, $[Cu(SCN)_4]^{2-}$, $[Cu(SCN)_5]^{3-}$; of these, the one which predominates according to the authors is the complex with an instability constant of $6.5 \cdot 10^{-6}$ at 18°.

Kitson [7] has suggested a spectrophotometric method of determining copper, cobalt, and iron in each others presence by means of ammonium thiocyanate in 50% aqueous acetone solution, to which potassium periodate is added for preventing reduction of Cu^{II}.

Thus the thiocyanate complexes of Cu^{II} have been studied, and also used for the quantitative determination of copper in aqueous acetone solution only. Accordingly, we thought it would be interesting, both from a practical and a theoretical point of view, to study the reaction of Cu^{II} ions with potassium thiocyanate in aqueous solution.

For preventing reduction of Cu^{II} ions, dilute solutions of hydrogen peroxide, ammonium or sodium persulfate, and nitric acid were used as oxidizing agents. The most suitable oxidizing agent for this purpose proved to be dilute nitric acid (pH about 3), which does not react with thiocyanate ions to form colored compounds.

Meta- and ortho-phosphoric acid were used as complexing agents for preventing reduction of Cu^{II} ions by thiocyanate ions in aqueous solution. In the presence of Cu^{II} and thiocyanate ions there is formed a stable compound with a yellow-green color. Apparently, this compound is a thiocyanate-phosphate complex.

The following materials were used: 1) freshly crystallized cupric sulfate; 2) potassium thiocyanate, chemically pure grade; 3) nitric acid (1 : 1); 4) zinc sulfate, chemically pure grade; 5) ferric sulfate, chemically pure grade; 6) aluminum sulfate, chemically pure grade; 7) metaphosphoric acid (saturated aqueous solution).

The copper content of the solution was determined iodometrically. The optical density of the solutions was measured on FEK-M and FNK-51 (blue filter) photoelectric colorimeters.

Interaction of Cupric Ions with Potassium Thiocyanate in the Presence of Nitric Acid

For establishing the effect of the amount of KSCN on its interaction with Cu^{II}, equal amounts of cupric sulfate and nitric acid, and various amounts of potassium thiocyanate (from 1 to 15 ml) were introduced into

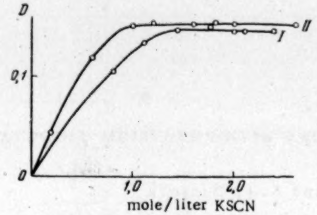

Fig. 1. The relation between the optical density of solutions of the copper thiocyanate complex, and the amount of potassium thiocyanate in the presence of nitric acid and metaphosphoric acid. Cupric sulfate concentration $1.2 \cdot 10^{-4}$ mole/liter Total volume of solution 25 ml: I) 0.2 ml of nitric acid (1 : 1) added; II) 1.0 ml of a saturated solution of metaphosphoric acid added.

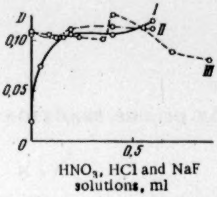

Fig. 2. The effect of HNO_3, HCl, and NaF on the optical density of the thiocyanate complex of divalent copper. Cupric sulfate concentration $1.6 \cdot 10^{-4}$ mole/liter, concentration of potassium thiocyanate 2.0 mole/liter. Total volume of solution 25 ml: I) HNO_3 (1 : 1) added; II) HCl (1 : 1) added; III) 1 N NaF added.

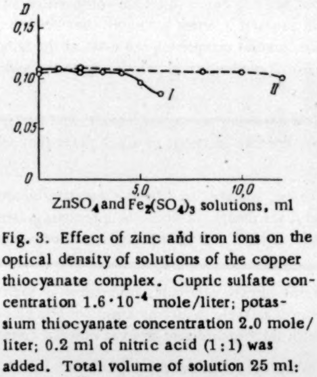

Fig. 3. Effect of zinc and iron ions on the optical density of solutions of the copper thiocyanate complex. Cupric sulfate concentration $1.6 \cdot 10^{-4}$ mole/liter; potassium thiocyanate concentration 2.0 mole/liter; 0.2 ml of nitric acid (1 : 1) was added. Total volume of solution 25 ml: I) $1.0 \cdot 10^{-5}$ mole/liter of $Fe(SO_4)_3$ added; II) 2.0 N $ZnSO_4$ solution added.

25 ml standard flasks. The solutions were made up to mark with water and then shaken; after 15 minutes their optical density was measured. As is evident from Fig. 1, with increasing potassium thiocyanate concentration, the optical density of the solutions increases up to a certain value and then remains constant.[*]

The effect of the amount of nitric acid for constant concentrations of Cu^{II} and potassium thiocyanate and the effect of hydrochloric acid on the optical density is illustrated in Fig. 2.

Addition of even small amounts of nitric acid sharply increases the optical density of the solution as compared with that of solutions to which no nitric acid has been added. Nevertheless, addition of more than 0.6 ml of nitric acid per 25 ml of solution increases the optical density of the solution even in the absence of copper; this can probably be explained by the formation of colored products by the interaction of nitric acid and potassium thiocyanate. Variations in amount of hydrochloric acid from 0.12 to 0.5 ml have almost no effect on the optical density. The presence of hydrochloric acid presumably does not affect the composition of the copper thiocyanate complex.

During a study of the effect of Zn^{2+} ions on the color of the copper thiocyanate complex, the zinc concentration was more than 100 times that of the copper concentration, as Fig. 3 shows (Curve 1); zinc ions do not interfere with the formation of the copper thiocyanate complex.

Over the concentration range studied in the case of iron ($4 \cdot 10^{-7} - 2.5 \cdot 10^{-6}$ g/ml), interference from iron was successfully suppressed by means of 2 N sodium fluoride solution (Fig. 3).

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[*] Very dilute potassium thiocyanate solutions do not give a color.

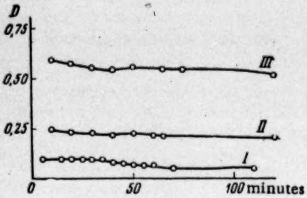

Fig. 4. Stability with time of the thiocyanate and phosphate-thiocyanate complexes of divalent copper. Total volume of solution, 25 ml.
I) Copper concentration $1.6 \cdot 10^{-4}$ mole/liter, potassium thiocyanate concentration $1.2 \cdot 10^{-4}$ mole/liter; 0.3 ml of 1 N sodium fluoride and 0.2 ml of nitric acid (1 : 1) added; II) copper concentration $1.6 \cdot 10^{-4}$ mole/liter, potassium thiocyanate concentration 1.2 mole/liter; 1 ml of a saturated solution of metaphosphoric acid added; III) copper concentration $4.0 \cdot 10^{-4}$ mole/liter, potassium thiocyanate concentration 2 moles/liter; 1 ml of a saturated solution of metaphosphoric acid added.

Results of measurements of the optical density of solutions of the cupric thiocyanate complex carried out at various sodium fluoride concentrations, show that the addition of large amounts of sodium fluoride lowers the color intensity of the solution; nevertheless, over a fairly extensive concentration range of the fluoride (0–0.5 ml of 1 N fluoride per 25 ml solution) the optical density of the solution is almost constant (Fig. 2, Curve III).

As Fig. 4 shows, the optical density of a solution of the thiocyanate complex of copper does not change in the course of 35 minutes.

As Fig. 5 shows, at concentrations of $5 \cdot 10^{-3} - 2.8 \cdot 10^{-2}$ g of Cu/liter, solutions of the complexes, in the presence of excess potassium thiocyanate, conform to the Beer law.

For low copper concentrations, this reaction is suitable for the photometric determination of copper in weakly nitric and hydrochloric solutions, in the presence of large amounts of zinc and small amounts of iron.

Interaction of Divalent Copper with Potassium Thiocyanate in the Presence of Metaphosphoric Acid

It was noted that the stability of the thiocyanate complex of Cu^{II} increases in the presence of metaphosphoric acid. Solutions of $CuSO_4$ containing metaphosphoric acid and potassium thiocyanate preserve their yellow-green color over a prolonged period. In the absence of metaphosphoric acid the color disappears rapidly, the solution gradually becomes turbid (when sufficient copper is present) while metaphosphoric acid prevents decolorization even in the presence of a reducing agent.

As the potassium thiocyanate concentration increases, the initial optical density of the solutions increases (Fig. 1), but, the higher the KSCN concentration, the greater the drop in optical density in the first minutes after mixing the solutions. It was observed, however, that after 15-20 minutes, the optical density assumes an equal value over a fairly wide potassium thiocyanate concentration range (Fig. 1).

Color stability is sufficient (Fig. 4) for using it for photometric measurements.

For copper concentrations of $2.5 \cdot 10^{-3} - 3.5 \cdot 10^{-2}$ g/liter the solutions obey Beer's law satisfactorily.

The color develops in moderately acid solution. At a pH of less than 1.8 the solution becomes turbid, while at a pH greater than 4 the solutions become decolorized. Maximum color intensity is achieved at a pH of 2-3. Substitution of meta- by orthophosphoric acid did not lead to any improvement. Potassium thiocyanate cannot be replaced by ammonium thiocyanate (because of the effect of ammonium ions).

The potassium thiocyanate must be added to the $CuSO_4$ solution after the addition of metaphosphoric acid. When KSCN is added to the $CuSO_4$ solution before metaphosphoric acid, rapid reduction of Cu^{II} to Cu^{I} with formation of a precipitate occurs; metaphosphoric acid, presumably, complexes Cu^{II} and thereby prevents its reduction. This is indirect proof of the fact that potassium thiocyanate does not react simply with the cupric ions, but with complex phosphate ions of Cu^{II}.

Chloride ions do not affect the color intensity at concentrations up to 0.15 g/ml, for a copper concentration of about 10^{-5} g/liter, i.e., at a limiting ratio of 15,000 : 1. At higher chloride concentrations, the optical density increases somewhat.

Aluminum does not affect the color intensity (solutions containing 250 times more aluminum than copper were tested); neither does zinc interfere.

The color of solutions of ferric thiocyanate does not disappear on addition of metaphosphoric acid to them, but only changes to a yellow-green, which is similar to the color of the phosphate-thiocyanate complex of divalent copper. Decolorization only occurs on raising the pH to 5, but, this, as indicated above, also leads to decolorization of the phosphate-thiocyanate complex of copper. Iron should not be present in solution in amounts which are twice that of the copper.

The results obtained show that the colored phosphate-thiocyanate complex of copper can be used for the photometric determination of copper in solutions containing large amounts of aluminum and zinc, and small amounts of iron. The sensitivity of the reaction is $2.5 \cdot 10^{-6} - 3.5 \cdot 10^{-5}$ g/ml.

Thus, determination of copper can be carried out both by means of its thiocyanate and phosphate-thiocyanate complexes. In both cases calibration curves are constructed within the coordinates: copper concentration – optical density. The latter is measured on a photocolorimeter provided with a blue filter.

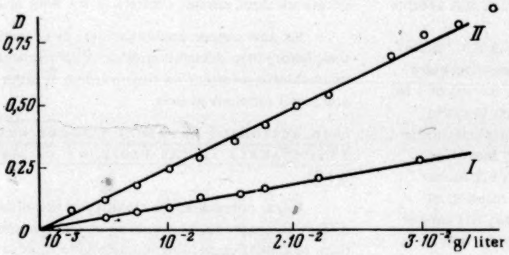

Fig. 5. Relation between the optical density of solutions of the thiocyanate and the phosphate-thiocyanate complexes of copper, and copper concentration (conformity to the Beer law).
I) Copper thiocyanate complex; II) copper phosphate-thiocyanate complex.

Standard solutions to be used for the first method are prepared by introducing from 1 to 5 ml of a $CuSO_4$ solution of known concentration (of the order of 10^{-4} mole/liter) into 25 standard flasks, 0.2 ml of HNO_3 (1 : 1) is then added, followed by 8 ml of 4 N KSCN, and 0.3 ml of 1 N NaF; the volume is made up to the mark with water, the flask shaken, and the optical density measured after 15 minutes.

The test solution is treated in the same way.

For the photometric determination of copper by the second variant involving metaphosphoric acid, the same procedure as that outlined above is followed, the sole difference in this case being the addition of 1 ml of saturated metaphosphoric acid instead of sodium fluoride, while the nitric acid is omitted.

SUMMARY

The reaction of cupric ions with potassium thiocyanate in aqueous solution has been studied.

Conditions have been established which guarantee the stability and high color intensity of the copper thiocyanate complex.

It has been shown that it is possible to use potassium thiocyanate for the photometric determination of copper in the presence of nitric and metaphosphoric acids. The reaction is more sensitive than that with ammonia and potassium ferrocyanide.

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THE ELECTROCHEMICAL BEHAVIOR OF AN ALUMINUM ELECTRODE DURING TITRATION OF ALUMINUM IONS WITH FLUORIDE

B. N. Kabanov and L. Ia. Pollak

During the potentiometric titration of aluminum ions by means of a sodium fluoride solution, using the classical method of Treadwell and Bernasconi [1], a small amount of a mixture of Fe^{3+} and Fe^{2+} ions is added in order to set up an oxidation–reduction system. Since the complex $[AlF_6]^{3-}$ is considerably more stable than the complex $[FeF_6]^{3-}$, then, in the course of titration, as long as there are aluminum ions in solution, sodium fluoride will be used up in forming a complex with aluminum. At the end point when all the aluminum ions have been complexed, formation of complex iron compounds starts, and, as a result of this, the potential of the platinum electrode is sharply displaced.

In 1948 an article by Chirkov appeared [2]; in the course of the work described there a successful attempt was made to use an aluminum electrode coupled with a nichrome electrode for the titration of aluminum with sodium fluoride. It is recommended that potentiometric titration of aluminum with sodium fluoride be carried out in a hydrochloric acid media, buffered at a pH of ~5 with sodium acetate, in the presence of sodium chloride.

This method has been used by Budanova and Volodarskaia [3] for the determination of aluminum in bronzes and brasses, and by Gorelova and Pollak [4] for the determination of aluminum in heat-resisting alloys based on nickel.

In all the papers indicated, only practical recommendations are given for the use of an aluminum-nichrome couple for the potentiometric determination of aluminum in various materials. Such questions as the mechanism of the operation of the electrode pair Al – NiCr, the reason for the potential jump at the end point when excess fluoride ions are present in solution, and the effect of cations and anions present in solution on the electrochemical behavior of the electrodes, are not discussed in the papers by S. K. Chirkov and the workers who followed him.

The purpose of the work discussed here was to study the electrochemical behavior of the aluminum electrode under conditions similar to those used during potentiometric titration.

EXPERIMENTAL

1. Potentiometric titration. The first point to settle was which of these two electrodes is the indicator electrode. For this purpose we carried out a compensation titration of an aluminum salt with the pairs NiCr – calomel electrode and Al – calomel electrode as in [4]. These experiments showed that the potential of the nichrome electrode remains constant during titration (Fig. 1, Curve 2), while the potential of the aluminum electrode changes sharply with changes in concentration of the F^- ions (Fig. 1, Curve 2). Thus, potential changes during titration, and the magnitude of the potential jump at the end-point, are determined by changes in the potential of the aluminum electrode only.

In order to clarify the mechanism of the aluminum electrode during potentiometric titration, the following questions must be resolved:

1) by what processes is the stationary potential of the aluminum determined in the given solutions;

2) the effect of accompanying anions (F^-, Cl^-, SO_4^{2-}, CH_3COO^-);

3) the mechanism of the sharp change in the potential of the aluminum electrode at the end-point during compensating and noncompensating potentiometric titration.

2. Polarization measurements. The aluminum electrode is not reversible, its potential is determined neither by the concentration of aluminum ions in solution, nor by the oxidation–reduction potential of the solution, but is usually determined by the relation between two different processes–cathodic and anodic. Such a potential is called stationary.

In order to establish the nature and rates of those anodic and cathodic processes which determine the stationary potential, and the potential of the aluminum electrode when current is flowing during potentiometric titration, polarization curves were taken for the aluminum electrode in pure solutions of sodium fluoride, and in the presence of additions of various salts (acetate, sulfate, and chloride) in various combinations.

The polarization curves on an aluminum electrode were taken by the usual compensation method using a saturated calomel electrode as the reference electrode. The technique used for taking the polarization curves has been described previously [5]. The potential of the polarized aluminum electrode was calculated with respect to the normal hydrogen electrode. Measurements were made at room temperature over the range 10^{-6} – 10^{-3} amp/cm^2 for the density of the polarizing current. Both electrodes (the polarized electrode–aluminum, and the auxiliary electrode–platinum) were placed in a hermetically sealed vessel with ground glass joints. Nitrogen was passed through the solution during the measurements to provide an inert atmosphere. Before each pair of curves (cathodic and anodic) was taken, the electrode was cleaned with glass powder or velvet emery paper, and then with wet and dry filter paper. On immersing the aluminum electrode in the test solution its stationary potential was measured, it was then subjected to polarization by an ever increasing current. Since the stationary potential of the aluminum electrode was not established immediately, the first measurement was made 2-3 minutes after immersion of the electrode in the test solution. The aluminum electrode used was in the form of aluminum wire of high purity (Mark 000) containing 99.999% Al.

Polarization measurements were made under conditions identical to those used for potentiometric titration, i.e., when the polarization curves were taken, the same salt concentration, and the same pH, were used as those adopted for potentiometric titration according to method [4].

In order to establish the effect of the anions Cl^-, CH_3COO^-, and F^-, taken separately and together, on the electrochemical behavior of an aluminum electrode during titration of aluminum, the polarization curves shown in Figs. 2-6* were taken.

DISCUSSION OF RESULTS

The following electrochemical reactions may take place on the surface of an aluminum electrode:

$H^+ + e = \frac{1}{2} H_2$ – discharge of hydrogen ions;

$Al = Al^{3+} + 3e$ – dissolution of aluminum.

Only these two processes occur on an aluminum electrode. When no current passes through the electrode and its potential does not change, then the rate at which hydrogen is evolved and the rate at which the metal will dissolve, will be equal to one another (the stationary state of the system) [6].

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*The concentrations indicated on the figures for the various salts were chosen on the basis of the following considerations.

0.5 N or 0.25 N sodium fluoride solutions are normally used for the potentiometric titration of aluminum. When the volume of solution to be titrated is about 100 ml, and if one assumes that at the end-point the excess sodium fluoride amounts to 0.1 ml, then the concentration of F^- ions at the end-point should be of the order of $\frac{0.1 \cdot 0.5}{100} = 0.5 \cdot 10^{-3}$ M. Accordingly, the concentration of F^- ions in the polarization measurements was 0.001 M.

Titration of aluminum is carried out in the presence of 10 g of NaCl for a total volume of about 80-100 ml. Consequently, the concentration of Cl^- ions in the test solution amounts to $\frac{10 \cdot 1000}{58.5 \cdot 100} \approx 2$ M.

The concentration of CH_3COO^- was calculated in similar fashion.

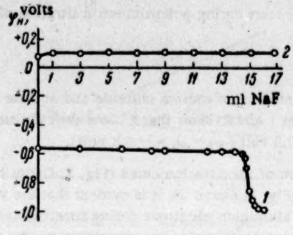

Fig. 1. Curves for the potentiometric titration of aluminum with sodium fluoride: 1) with the electrode pair Al–calomel electrode; 2) with the electrode pair NiCr–calomel electrode.

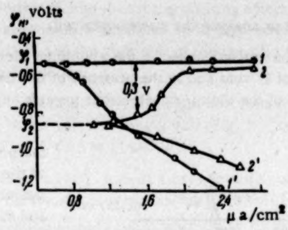

Fig. 2. Polarization curves of the aluminum electrode in the solutions: 1) 2 N NaCl + 1 N CH_3COONa; 2) 0.001 N NaF + 2 N NaCl + 1 N CH_3COONa.

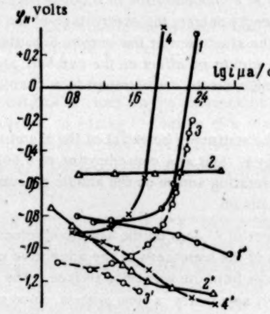

Fig. 3. Polarization curves for an aluminum electrode in solutions of: 1) 0.001 N NaF + 1 N CH_3COONa; 2) 0.001 N NaF + 2 N NaCl; 3) 0.001 N NaF; 4) 0.001 N NaF + N Na_2SO_4.

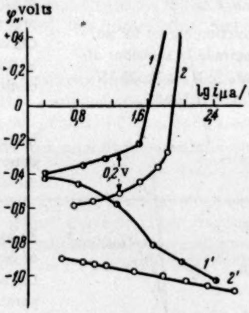

Fig. 4. Polarization curves for an aluminum electrode in solutions of: 1) 0.001 N NaF; 2) 2 N NaCl; 3) 1 N NaF + 1 N Na_2SO_4 + 1 N CH_3COONa.

Dissolution of the metal is shown graphically by the anodic polarization curve, while liberation of hydrogen is shown by the cathodic curve. The point of intersection of the extrapolated cathodic and anodic polarization curves gives the value of the stationary potential of the electrode (Fig. 7).

We measured the stationary potentials of the aluminum electrode during titration in the given solution. The question is, what explains the shift in the stationary potential towards negative values during titration of aluminum with fluoride ions. One of the following cases is possible:

1) the stationary potential is shifted as the result of an acceleration of the anodic process (a decrease in the overvoltage of the process of aluminum dissolution);

2) the stationary potential is shifted as the result of a slowing down of the cathodic process (an increase in hydrogen overvoltage);

3) the stationary potential is shifted as a result of both processes occurring simultaneously.

It is accordingly necessary to establish which of these cases occurs during potentiometric titration of aluminum with sodium fluoride.

Let us analyze the curves obtained.

Polarization curves for the aluminum electrode taken in a mixture of sodium chloride and acetate in the absence of F^- ions and in the presence of the latter (Fig. 2, Curves 1 and 2) show that F^- ions shift the stationary potential of the aluminum electrode towards negative values by 0.3 volt ($\varphi_2 - \varphi_1 = -0.3$ volt).

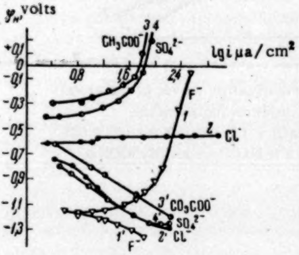

Fig. 5. Polarization curves for an aluminum electrode in solutions of: 1) 0.001 N NaF; 2) N NaCl; 3) 1N CH_3COONa; 4) 1 N Na_2SO_4.

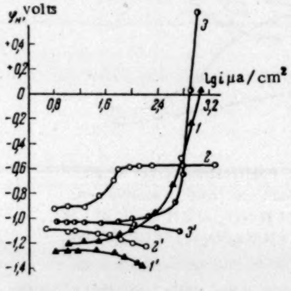

Fig. 6. Polarization curves for an aluminum electrode in solutions of: 1) 0.01 N NaF; 2) 0.01 N NaF + 2N NaCl; 3) 0.01 N NaF + 1 N CH_3COONa.

From a comparison of the titration curve (Fig. 1, Curve 1) and the polarization curve (Fig. 2, Curve 2), it is evident that the values of the potentials of the aluminum electrode during titration and the stationary potentials during polarization measurements are the same, and that, in addition, the potential jump at the end-point is equal in magnitude to the shift in the stationary potential of the aluminum electrode during polarization measurements. For a detailed explanation of the reason for the shift in the stationary potential of the aluminum electrode by 0.3 volt under the influence of F^- ions, it is necessary to consider the effect of each of the anions present on the shape of the cathodic and anodic overvoltage curve.

F^- Ions. a) F^- ions at a concentration of 0.001 N (in the presence of Cl^- and CH_3COO^-) strongly depress the overvoltage of the anodic process of dissolution of the aluminum at low current densities (Fig. 2, Curves 1 and 2) and have almost no effect on the cathodic process (Fig. 2, Curves 1' and 2'). Similar results are obtained for a fluoride concentration of 0.01 N.

Thus, the shift in the stationary potential of the aluminum electrode of 0.3 volt caused by F^- ions at a concentration of 0.001 N, is determined by their accelerating action on the anodic process only—the dissolution of the aluminum.

This activating effect of F^- ions on the aluminum electrode can be explained on the basis of the hypothesis of the adsorptive expulsion of oxygen by fluoride atoms from the electrode surface. The activating adsorption of F^- ions is apparently a slow process, since at comparatively high densities of the anodic current the aluminum, in the absence of chloride ions, is completely passivized (Fig. 3, Curve 1; Fig. 4, Curve 2; and Fig. 5, Curve 1).

b) F^- ions in the presence of SO_4^{2-} and CH_3COO^- ions shift the stationary potential of the aluminum electrode both at the expense of the anodic and cathodic processes (Fig. 4). Thus the mechanism of the shift in the stationary potential caused by F^- ions is different in the presence of Cl^- (Fig. 2) and SO_4^{2-} ions respectively.

c) F^- ions cause the highest hydrogen overvoltage on the aluminum (Fig. 3, Fig. 5, Curves 1', 2', 3', and 4') as compared with the other test ions.

Cl^- Ions. a) In the absence of chloride ions, during anodic polarization of the aluminum electrode, starting at a current density of about 10^{-4} amps/cm^2, there occurs a sharp shift in the potential toward positive values (complete passivization of the aluminum) (Fig. 3, Curves 1, 3, and 4; Fig. 4, Curves 1 and 2 etc.).

In the presence of Cl^- ions this phenomenon is not observed, Cl^- ions prevent anodic passivization of the aluminum electrode (Fig. 2, Curves 1 and 2; Fig. 3, Curve 2 etc.). The mechanism of the activating effect of Cl^- ions on iron and magnesium electrodes during anodic polarization has been studied several times [6].

It is worthy of note that the activating effect of chloride ions on aluminum is preserved up to high current densities; this testifies to the high rate of the specific adsorption of the chloride ions.

b) Cl^- ions depress the hydrogen overvoltage in 0.01 N and 0.001 N NaF solution by 0.2 volt (Fig. 3, Curves 2' and 3', and Fig. 6, Curves 1' and 2').

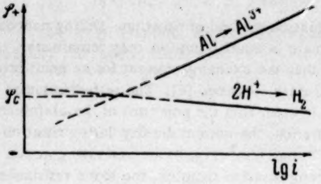

Fig. 7. Establishment of the stationary potential on an aluminum electrode.

SO_4^{2-} Ions. a) SO_4^{2-} ions at a concentration of 0.1 N also depress the hydrogen overvoltage by 0.2 volt in 0.001 N fluoride solution (Fig. 3, Curves 3' and 4') this could be the result of partial expulsion of F^- from the aluminum surface.

b) SO_4^{2-} ions lower the current density at which the passivized increase in the anodic curve occurs (Fig. 3, Curves 3 and 4), i.e., they decrease the activating effect of the F^- ions.

CH_3COO^- Ions. a) CH_3COO^- ions lower the hydrogen overvoltage on aluminum in 0.001 N NaF by 0.3-0.35 volt (Fig. 3, Curves 1' and 3'; Fig. 6, Curves 1' and 3'), obviously, as a result of high specific adsorption on aluminum.

b) CH_3COO^- ions in the presence of SO_4^{2-} ions, at low current densities, give the lowest hydrogen overvoltage (Fig. 4, Curve 1'; Fig. 5, Curve 3'). Accordingly, the use of SO_4^{2-} ions instead of Cl^- ions cannot be recommended.

c) CH_3COOH^- ions (in the presence of Cl^- ions) increase the sensitivity of the aluminum electrode to F^- ions. Actually, on adding F^- ions up to a concentration of 0.001 N to a solution of 2 N NaCl + 1 N CH_3COONa, a shift in potential of 0.3 volt is observed (Fig. 2, Curve 2), while on addition of F^- ions up to a concentration of 0.001 N to a solution of 2 N NaCl which does not contain acetate ions, no shift in potential is observed at all (Fig. 3, Curve 2).

When the concentration of F^- ions is increased to 0.001 N, then a shift in potential of 0.3 volt is also observed in the solution of 2 N NaCl which does not contain acetate (Fig. 6, Curve 2). Thus, fluoride activates aluminum at low current densities, chloride prevents complete passivization, thereby increasing the potential range over which the fluoride ions are active, while acetate ions increase the activating effect of fluoride ions in the presence of chloride ions.

From what has been said it follows that the change in potential of the aluminum electrode during potentiometric titration (2, 3, 4) is the result of a combination of the effect of the anions listed, on the electrochemical behavior of the aluminum electrode.

All that has been said above relates to compensation potentiometric titration of aluminum with sodium fluoride solution using the aluminum indicator electrode. In the case of noncompensation titration, both electrodes—aluminum and nichrome—are directly immersed in the solution being titrated and are connected to the poles of a sensitive galvanometer. A resistance of 15-20 thousand ohms is connected in series in the circuit; thus, during titration, a current of the order of $5 \cdot 10^{-5}$ amps [*] passes through the circuit.

Since the aluminum electrode has a higher negative potential than the nichrome electrode, it is polarized anodically. Consequently, for characterization of the behavior of the aluminum electrode during noncompensation titration, the anodic polarization curve is of significance, and the potential jump at the end-point is determined only by the decrease in the value of the anodic overvoltage.

Thus, the potential jump at the end-point during both compensation and noncompensation titration of aluminum by sodium fluoride, is basically determined by the same reason—acceleration of anodic dissolution of aluminum.

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[*] The potential difference between the aluminum and nichrome electrodes at the moment of compensation, in the absence of a current, is 1 volt as is evident from Fig. 1. Nevertheless, during noncompensation titration this value may decrease a few times because of the polarization of the electrodes.

The mechanism of the shift in potential under the influence of F^- ions is the same for both compensation and noncompensation titration in the case under discussion.

We can establish the limits of applicability of the noncompensation method of titration. During noncompensation titration, the potential of the indicator electrode may remain in equilibrium, or may remain stationary in the case where the current density during titration is less than the exchange current for an equilibrium electrode or less than the self-dissolution current in the case of stationary electrode [6]. The self-dissolution current, as is evident from Fig. 2, is equal to $1.1 \cdot 10^{-5}$ amps/cm^2. In order that the potential of the aluminum electrode should remain stationary even during noncompensation titration, the current density during titration should be less than this value. At current densities greater than 10^{-4} amps/cm^2 (Fig. 2) the activating action of the fluoride ions almost disappears. Accordingly, if, during noncompensation titration, too low a resistance R, less than $R = S \cdot 10{,}000$ ohms is included in the circuit, where S is the surface area of the immersed part of the aluminum electrode, then the potential shift under the influence of fluoride ions at a concentration of 0.001 N is one tenth the shift which is observed during compensation measurements of potential.

All that has been said above relates to the behavior of an aluminum electrode in solutions of salts sodium chloride, acetate, sulfate, and fluoride). Since it is anions which mainly affect the corrosion of aluminum, we first studied their effect on the electrochemical behavior of the aluminum electrode. As mentioned already, the method studied is applicable to the study of heat-resistant alloys, which are made up of a complex mixture of a large number of elements (nickel, chromium, aluminum, molybdenum, tungsten, titanium, iron and other elements present as impurities). A large fraction of the cations present in the alloys possess variable valence. The possibility is not excluded that certain cations also affect the behavior of the aluminum electrode by altering the specific adsorption of the anions. This testifies to the need for an independent study of the question of the effect of cations on the electrochemical behavior of aluminum.

SUMMARY

1. It has been demonstrated that during titration of aluminum salts by sodium fluoride solution using an aluminum-nichrome electrode pair, the potential "shift" at the end-point is caused by a sharp change in the stationary potential of the aluminum electrode (indicator electrode); the potential of the nichrome electrode does not change during titration.

2. In order to establish the nature of the anodic and cathodic processes which determine the stationary potential of the aluminum electrode, and its change during titration, polarization curves were taken for the aluminum electrode in solutions of F^- ions in the presence of Cl^-, CH_3COO^-, and SO_4^{2-} ions for various combinations of these ions, and at concentrations of these ions which correspond to those used for titration of aluminum salts with fluoride.

3. It has been shown that the sharp shift in potential to negative values at the end-point is caused by the accelerating effect of F^- ions on the anodic dissolution of aluminum (by activation of the aluminum electrode); fluoride ions have hardly any effect on cathodic liberation of hydrogen.

4. Cl^- ions prevent complete passivization of the aluminum, and thereby increase the potential range over which F^- ions are active. CH_3COO^- ions increase the sensitivity of the aluminum electrode to F^- ions.

5. The reason for the potential shift of the aluminum electrode at the end-point under the influence of F^- ions is the same for both compensation and noncompensation methods of titration.

6. The limits of the applicability of the noncompensation method have been established with respect to the range of current density in which the fluoride ions exhibit an activating influence on the aluminum electrode.

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QUANTITATIVE DETERMINATION OF THALLIUM AS THE DICHROMATE

COMMUNICATION 1. GRAVIMETRIC AND VOLUMETRIC METHODS

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Quantitative determination of scattered metals, in particular thallium, is connected with considerable difficulties. These difficulties are the result of the necessity of determining scattered metals in the presence of large amounts of the elements accompanying them [1, 2]. When the concentration of thallium in the test material is very low, it is necessary to resort to preliminary chemical enrichment by extraction methods [3-14], cementation [15], chromatography [16-17], precipitation [2, 18-20] or by coprecipitation both by organic [21], and inorganic [22] reagents. In those cases where the concentration of the thallium is sufficient for its direct determination by chemical analytical methods, methods of determining thallium are necessary, which simultaneously ensure its complete separation from accompanying elements.

In the vast literature on the analytical chemistry of thallium, there are no references to methods which would fully satisfy these requirements, despite the fact that methods are known for the determination of thallium which are based on reactions specific for this metal, for example, on precipitation reactions [23-25]. Accordingly, determination of thallium is usually preceded by its separation from interfering elements.

The gravimetric methods which have been suggested in recent years for the determination of thallium [25-27] require reagents which are not readily available, and the use of which in analytical practice meets several difficulties. The best gravimetric method for determination of thallium, as acknowledged by many workers [15, 28-29], is the classical chromate method, which is based on precipitation of thallium from ammoniacal solutions by potassium chromate. Nevertheless, in the presence of other metals, the chromate method is only applicable in certain cases. In such cases the elements which interfere with determination of thallium are kept in solution, either by altering their valence state by means of preliminary oxidation (under conditions which exclude the oxidation of thallium) [28], or by the formation of soluble complexes [18, 19, 28, 30-32]. The manner in which the chromate method is used depends on the nature of the metal which is present, and when several metals are present simultaneously, the method is not always applicable. In order to form soluble complexes of the accompanying elements, it is often necessary to use various complexing agents, the simultaneous use of which is not always possible. Thus, the simultaneous presence of trivalent thallium and iron, which interfere with the determination of univalent thallium in the form of the chromate, excludes the possibility of using an alkali metal cyanide and sulfosalicylic acid which are recommended for complexing them [33].

It was found necessary therefore to study the possibility of carrying out a quantitative determination of thallium as its dichromate during its precipitation from acid solutions. This method of determining thallium could be simultaneously used for its separation from all metals which do not form insoluble compounds under the given conditions.

The possibility of combining the quantitative determination of thallium as its dichromate with its separation from a large number of accompanying elements is of undoubted interest.

Published information on thallium dichromate is scant and dates in the main from the last century [34-39]. Potassium dichromate is a sparingly soluble compound which separates out from solution more readily the chromate [37]. The similarity of thallium mono- and dichromates gave Carstanjen [37] a basis for suggesting that both compounds could be used for the quantitative determination of thallium.

The microcrystalloscopic method of detecting thallium [40-41] which is based on the formation of crystals of thallium dichromate, is characterized by a limit of identification of about 1 γ at a limiting concentration of 1 : 50,000 [41].

In a paper [42] devoted to the iodometric determination of thallium during its precipitation from alkaline solutions in the form of the monochromate, among other results, results are given of two parallel precipitations of thallium by potassium chromate in the presence of dilute sulfuric acid; in this case 99.53% of the thallium taken was found, when calculations were based on thallium dichromate.

Despite these separate observations, thallium dichromate has been regarded as an unsuitable form for quantitative determination [33]. Forcheimer and Epple [33] tried to precipitate thallium quantitatively as the dichromate from solutions of varying concentration of perchloric acid, but the results obtained were not reproducible. Thallium was only precipitated completely from 1 N perchloric acid when the solution was kept at 0° overnight before filtering. It has been suggested [33] that the high results obtained for the determination of thallium may be explained by the formation of thallium polychromates; and low results by the formation of precipitates consisting of mixtures of thallium mono- and dichromate. These suggestions were probably made because of the absence of published information on the systematic study of thallium chromates. Neither their conditions of formation or their physicochemical properties were known with any certainty.

It has been considered that it is impossible to weigh thallium as its dichromate, Forcheimer and Epple [33] precipitated thallium by means of sodium chromate from a solution of perchloric acid under strictly defined condiditons, only for the separation of univalent thallium from trivalent thallium and from iron when all were present simultaneously. For the quantitative determination of thallium, the precipitate of thallium dichromate was converted into thallium monochromate [33] by treating the dichromate on the filter with ammonia solution containing sodium chromate and cyanide.

In order to establish the composition of the thallium chromates, and the concentration limits within which each of them exists, the system $Tl_2CrO_4-CrO_3-H_2O$ was studied by the method of isothermal solubility, while a study was also made of the interactions which occur in the mutual system formed by potassium chromate and sulfuric acid. In the course of this work it was first of all established that, in particular, thallium dichromate Tl_2CrO_7 is an incongruently soluble compound which is completely precipitated by excess chromic anhydride. The results obtained served as a theoretical basis for a detailed development of a method for the quantitative determination of thallium as its dichromate.

In the work described here a study was made of the precipitation of thallium as $Tl_2Cr_2O_7$ from neutral and sulfuric acid solution by means of chromic anhydride.

In order to determine the conditions necessary for the quantitive precipitation of thallium, it was necessary to establish the relationship between the solubility of potassium dichromate and the various ratios of sulfuric acid to chromic anhydride in solution. For this purpose, the same amount of thallium was precipitated by means of chromic anhydride of varying concentration. Precipitation of thallium by chromic anhydride of the same concentration was carried out from a series of sulfuric acid solutions of varying concentrations.

The completeness of precipitation of thallium was determined volumetrically on the basis of the amount of chromic anhydride which had reacted, and by a gravimetric method. The results of these determinations, at the same time, served as a basis for establishing the conditions required for the quantitative determination of thallium by these methods.

The volumetric method, which does not require quantitative separation of the solid phase from the liquid phase, was at the same time a necessary prerequisite for developing a gravimetric method of determining thallium, since, in this case, the problem was complicated by the necessity of washing the precipitate of thallium dichromate in order to preserve its composition.

The Volumetric Method

The method is based on precipitation of thallium as dichromate from neutral or acid solutions by means of chromic anhydride. Thallium was determined on the basis of the amount of chromic anhydride which had thereupon reacted, the concentration of the chromic anhydride having been determined iodometrically.

TABLE 1

Volumetric Determination of Thallium During Its Precipitation as the Dichromate (0.2062 g of Tl taken)

Am't. taken in g per 100 ml		CrO_3 concentration in mother liquor, g/100 ml	Tl found, in g	Error	
CrO_3	H_2SO_4			in mg	in %
0,1535	—	0,0533	0,2049	−1,3	−0,63
0,2371	—	0,1362	0,2062	0,0	0,0
0,2371	0,3	0,1362	0,2062	0,0	0,0
0,2371	1,0	0,1375	0,2036	−2,6	−1,26
0,2371	10,0	0,1407	0,1970	−9,2	−4,46
0,2859	—	0,1850	0,2062	0,0	0,0
0,2859	0,3	0,1851	0,2058	−0,4	−0,19
0,2859	1,0	0,1856	0,2049	−1,3	−0,63
0,3177	—	0,2166	0,2066	+0,4	+0,19
0,3177	0,3	0,2168	0,2062	0,0	0,0
0,3177	1,0	0,2168	0,2062	0,0	0,0
0,3177	10,0	0,2175	0,2048	−1,4	−0,68
0,3337	—	0,2328	0,2062	0,0	0,0
0,3337	0,3	0,2330	0,2058	−0,4	−0,19
0,3367	1,0	0,2359	0,2060	−0,2	−0,10
0,3967	—	0,2960	0,2058	−0,4	−0,19
0,3967	0,3	0,2958	0,2062	0,0	0,0
0,3967	1,0	0,2958	0,2062	0,0	0,0
0,4770	—	0,3761	0,2062	0,0	0,0
0,4770	0,3	0,3761	0,2062	0,0	0,0
0,4770	1,0	0,3761	0,2062	0,0	0,0
0,4902	10,0	0,3900	0,2048	−1,4	−0,68

Earlier [43, 42], thallium had been determined volumetrically by its precipitation from alkaline solutions as the monochromate. This method has been recommended for the quantitative determination of thallium [42].

The drawback of the volumetric method is the indirect determination of thallium, particularly in view of the large difference in the atomic weights of thallium and chromium. Naturally, this drawback is not quite so important in the case of precipitation of thallium as the dichromate, as in the case of its precipitation as the chromate. Nevertheless, even during precipitation of thallium as the dichromate, all the operations must be carried out carefully in the volumetric method.

The original solution of thallium sulfate contained 0.2062 g of thallium in 10 ml. The concentration of chromic anhydride varied within the limits 0.15 to 0.49 g in 100 ml. The sulfuric acid concentration range was 0.3, 1 and 10 g in 100 ml. In those cases where precipitation of thallium was carried out without addition of sulfuric acid, its concentration in the mother liquor was determined on the basis of the amount of material which had reacted, and amounted to 0.05 g per 100 ml of solution.

Aliquot portions were taken and titrated by means of microburets. To 10 ml of the original solution contained in a 100 ml standard flask was added the appropriate amounts of sulfuric acid and standard chromic anhydride solutions. The solution plus the precipitate of thallium dichromate was left overnight. Excess chromic anhydride was then determined on an aliquot of the filtrate. The amount of chromic anhydride which had reacted with thallium was calculated by difference. Each series of precipitations of thallium by the same amount of chromic anhydride was carried out in one standard flask. In order to avoid errors in the determination of the original concentrations of the chromic anhydride, connected with conversion of the various amounts of the standard solution to 100 ml, their concentration was established directly in the same flask as that used for a given series of precipitations. Iodometric determination of chromic anhydride was carried out under conditions ensuring absence of free iodine in sulfuric acid solutions of potassium iodide, this being controlled by carrying out parallel tests. The thiosulfate normality was of the order of 0.05.

The results obtained (Table 1) show that it is possible to carry out a quantitative volumetric determination of thallium during its precipitation as the dichromate from neutral and acid solutions by means of chromic anhydride. In such determinations, the acidity of the solution must be taken into account. When original solution contains up to 0.3 g of sulfuric acid per 100 ml, a content of 0.14 g of chromic anhydride per 100 ml of mother liquor is sufficient to guarantee quantitative precipitation of thallium. When the original solution contains 1 g of sulfuric acid per 100 ml, the thallium is quantitatively precipitated by a chromic anhydride content in the liquid phase of a minimum of 0.22 g CrO_3. Quantitative precipitation of thallium was not observed in the case of solutions containing 10 g of sulfuric acid per 100 ml of solution, for all the chromic anhydride concentrations examined, since, in such cases, a large excess of CrO_3 is required. All the same, volumetric determination of thallium at high concentrations of chromic anhydride cannot guarantee the necessary accuracy.

Accordingly, in practice, it is expedient during the volumetric determination of thallium, to precipitate the latter as its dichromate from solutions containing up to 1 g of sulfuric acid per 100 ml. Under such conditions, the chromic anhydride concentration of the mother liquor should amount to, on an average, about 0.25 g per 100 ml solution.

Gravimetric Method

One of the requisite conditions for using thallium dichromate as a gravimetric form is that it should be quantitatively precipitated from the mother liquor, and that its composition should be constant.

Thallium dichromate is an incongruently soluble compound with a constant composition. It has been established experimentally that this compound is insoluble, particularly in acetone and ethanol. Consequently, it can be assumed that when thallium dichromate is washed by the solvents mentioned, its composition will not change. Quantitative chemical analysis of thallium dichromate is not accurate enough to establish whether or not small changes in its composition do, in fact, occur under such conditions. Accordingly, in order to investigate thallium dichromate washed with acetone or ethanol, use was made in particular of phase differential thermal analysis. A knowledge of the thermal characteristics of thallium dichromate is also essential for enabling a correct choice to be made of the conditions to be used for drying it to constant weight.

Thermographic Study of Thallium Dichromate

Differential thermal investigation of thallium dichromate was carried out on a registering pyrometer of the N. S. Kurnakov type, using a chromel-alumel thermocouple. The thermograms obtained for thallium dichromate washed with acetone and ethanol are shown in Fig. 1. In Fig. 2 are shown respectively the thermogram obtained for thallium dichromate carefully removed from mother liquor by means of a filter, and thallium dichromate washed first with water and then with acetone.

As these thermograms show, the heating curves for thallium dichromate washed with the two solvents (Fig. 1) are exactly the same, and are characterized by the presence of two endothermic effects. As visual observation of the heating process showed, the thermal effect observed at 354-358° corresponds to the first appearance of a liquid phase. The second effect which occurs during the range 358-365° corresponds to complete fusion. This indicates that thallium dichromate melts with decomposition according to a peritectic reaction. Up to the point of incipient melting thallium dichromate is thermally stable.

The heating curve for unwashed thallium dichromate (Fig. 2a) which, consequently, contains some dry residue from the mother liquor, is also similar to the curves already considered; the only difference is that the endothermic effect in this case naturally occurs at a lower temperature.

The similarity of the thermograms obtained indicate that thallium dichromate does not change its composition on washing with acetone or ethanol.

The heating curve for thallium dichromate washed with water (Fig. 2b) is characterized by a small, additional endothermic effect which occurs in the solid state at a temperature of 330-335°. This effect corresponds to a polymorphic transformation of thallium monochromate which is fixed thermographically during its heating. Consequently, the thermogram for thallium dichromate washed with water is a record of the behavior of a mixture of thallium mono- and dichromate. This testifies to decomposition of thallium dichromate as a consequence of incongruent dissolution.

The results obtained show that acetone and ethanol can be used successfully for washing thallium

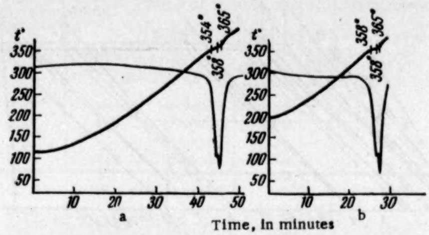

Fig. 1. Heating curves for thallium dichromate washed with acetone (a) and ethanol (b).

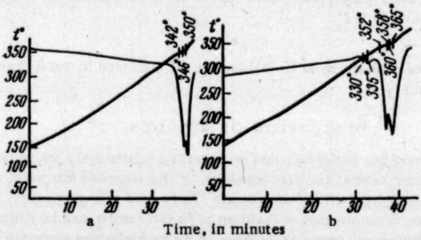

Fig. 2. Heating curves for thallium dichromate removed directly from the mother liquor (a), and washed first with water and then with acetone (b).

dichromate free from chromic anhydride. For this purpose, the concentration of the chromic anhydride should be low so as not to lead to interaction with the organic solvents.

Gravimetric determination of thallium as the dichromate under various precipitation conditions. Ten ml of a solution containing 0.1 g of thallium sulfate was used for the precipitation conditions. Sulfuric acid was added, and a standard solution of chromic anhydride added while the solution was gently warmed. The volume was then made up to 100 ml, the solution was finally left to cool to room temperature and then left overnight.

The sulfuric acid concentration in the various tests was 0.3, 1, 10, 18, and 25 g per 100 ml of solution. In those cases where precipitation was carried out from neutral solutions, the sulfuric acid concentration was determined from the amount of materials which had reacted, and amounted to 0.02 g. The chromic anhydride concentration of the solution was varied from 0.25 to 10 g per 100 ml of solution. The precipitate of thallium dichromate was filtered through a No. 4 crucible. When precipitation was effected by means of chromic anhydride, the concentration of which was greater than 1 g per 100 ml of solution, the precipitate of thallium dichromate was washed beforehand with a solution of chromic anhydride of the same concentration as that in the mother liquor in the case where precipitation was carried out from sulfuric solutions; the precipitate was then washed with a solution containing 1 g of CrO_3 per 100 ml of solution, and then with acetone until the chromate could not be detected iodometrically in the wash liquors. The washed precipitate of thallium dichromate was dried to constant weight at 110-130°.

In those cases where the error in determining thallium was considerable as a result of incomplete precipitation, the solution containing the precipitate was cooled to 1-3° for 2-4 hours.

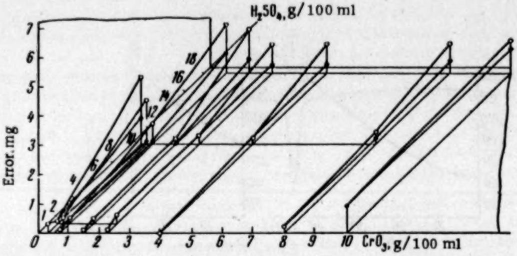

Fig. 3. Relation between the experimental error in determining thallium as its dichromate and the concentration of sulfuric acid and chromic anhydride:
○) $Tl_2Cr_2O_7$ precipitate kept in the mother liquor for 18-20 hours at room temperature; ●) $Tl_2Cr_2O_7$ precipitate kept in the mother liquor for 2-4 hours on cooling to 1-3°.

Results for the determination of thallium as its dichromate are presented in Table 2 and are illustrated by the three-dimensional diagram in Fig. 3.

DISCUSSION OF RESULTS

The work described above testifies to the fact that thallium is quantitatively precipitated in the form of $Tl_2Cr_2O_7$ by the dichromate ion from neutral and acid solutions. In the course of this work, it was established that, in contrast to published results [33], thallium dichromate can be used as a gravimetric form. In addition it has been shown that quantitative determination of thallium as its dichromate can be carried out over a large concentration range of acid in solution and over a wide range of the precipitating chromate.

By using the gravimetric technique of determining thallium, it was found that it was possible to extend the concentration ranges of the sulfuric acid and chromic anhydride considerably, as compared with the concentrations of these reagents used for the volumetric technique during precipitation of thallium dichromate. The experimental error in determining thallium as its dichromate depends on the ratio of sulfuric acid to chromic anhydride in solution. For the quantitative precipitation of thallium, the concentration of acid and chromic anhydride should not exceed certain definite limits established in the course of the present work.

Comparison of the results obtained for thallium (Table 2) when the solution containing the precipitate of thallium dichromate was cooled, and when the solution was kept at room temperature, shows that, as a consequence of the decrease in solubility of the thallium dichromate with the drop in temperature, the experimental error in determining thallium decreases with cooling. When cooling is used, quantitative results are obtained for thallium which are not obtained when cooling is omitted.

The maximum concentration of chromic anhydride which ensures quantitative precipitation of thallium dichromate, both from neutral and sulfuric acid solutions, amounts to approximately 8 g per 100 ml of solution. It is characteristic that when 10 g of chromic anhydride is used, the experimental error, which testifies to incomplete precipitation of thallium, remains almost unchanged even in those cases where precipitation is carried out with cooling (Table 2).

In order to precipitate thallium quantitatively as its dichromate from acid solutions, a greater excess of chromic anhydride is required the higher the acid concentration. When thallium dichromate is precipitated by the same amount of chromic anhydride from solutions with varying sulfuric acid concentrations, the experimental error in determining thallium increases with increasing acid concentration. This is clearly shown in Fig. 3.

The permissible sulfuric acid concentration for determination of thallium as the dichromate amounts to

TABLE 2

Gravimetric Determination of Thallium as Its Dichromate
(0.0810 g of Tl taken)

Amount taken in g per 100 ml		Time of contact of precip. with mother liquor			
		18-20 hrs at room temp.		2-4hrs on cooling to 1-3°	
CrO_3	H_2SO_4	Tl found,* in g	error in mg	Tl found,* in g	error in mg
0,25	—	0,0808	—0,2	—	—
0,25	0,3	0,0808	—0,2	—	—
0,35	—	0,0807	—0,3	—	—
0,35	0,3	0,0808	—0,2	—	—
0,35	1	0,0809	—0,1	—	—
0,35	10	0,0787	—2,3	0,0801	—0,9
0,40	1	0,0808	—0,2	—	—
0,40	10	0.0786	—2,4	0,0803	—0,7
0,40	18	0,0764	—4,6	0,0777	—3,3
0,55	1	0,0808	—0,2	—	—
0,55	10	0,0795	—1,5	0,0809	—0,1
0,65	1	0,0810	0,0	—	—
0,65	10	0,0797	—1,3	0,0808	—0,2
0,75	—	0,0809	—0,1	—	—
0,75	1	0,0808	—0,2	—	—
0,75	10	0,0803	—0,7	0,0809	—0,1
0,75	18	0,0793	—1,7	0,0803	—0,7
1,5	—	0,0809	—0,1	—	—
1,5	1	0,0809	—0,1	—	—
1,5	10	0,0808	—0,2	0,0810	0,0
1,5	18	0,0795	—1,5	0,0805	—0,5
2,25	—	0,0809	—0,1	—	—
2,25	1	0,0807	—0,3	—	—
2,25	10	0,0807	—0,3	—	—
2,25	18	0,0800	—1,0	0,0807	—0,3
4,0	—	0,0810	0,0	—	—
4,0	10	0,0808	—0,2	—	—
4,0	18	0,0800	—1,0	0,0807	—0,3
8,0	—	0,0808	—0,2	—	—
8,0	10	0,0806	—0,4	0,0808	—0,2
8,0	18	0,0800	—1,0	0,0807	—0,3
10,0	—	0,0802	—0,8	0,0801	—0,9
10,0	18	0,0799	—1,1	0,0802	—0,8
8,0	25	0,0799	—1,1	0,0802	—0,8

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*Mean results are given for several cases which were in good agreement with each other.

approximately 18 g/100 ml of solution. Quantitative precipitation of thallium is observed under these conditions only when the solutions are cooled. When thallium dichromate is precipitated from solutions containing 25 g of sulfuric acid per 100 ml by means of chromic anhydride of the maximum permissible concentration, the experimental error obtained indicates incomplete precipitation of thallium, independently of the fact whether the solutions are cooled or not (Table 2).

The experimental error of all determinations, is on the average the same, consequently, the changes in experimental error in thallium determination as a function of the varying concentrations of sulfuric acid and chromic anhydride, are determined by the solubility of thallium dichromate under the given conditions.

The experimental data obtained (Table 2) enables one to choose, for each special case, the necessary concentration of chromic anhydride as a function of the acid concentration of the solution for the quantitative precipitation of thallium.

In general it is best to precipitate thallium as its dichromate from solutions containing up to 10 g of sulfuric acid per 100 ml of solution, by means of chromic anhydride whose concentration amounts to, on an average, 1-2 g per 100 ml of the liquid phase. The precipitate of thallium dichromate plus mother liquor is cooled for 3-4 hours to 0-3°. It is desirable that the total volume of the solution should not exceed 100 ml under these conditions. The thallium dichromate is filtered through a No. 4 crucible and washed with a cooled solution of chromic anhydride whose concentration is the same as that in the original solution, and then with a solution containing 0.25 g of CrO_3 in 100 ml, and finally with acetone or ethanol until no chromate can be detected in the wash liquor. The thallium dichromate is dried to constant weight at 110-130°.

Results of thallium determination by this method are given in Table 3. The sulfuric acid concentration as well as that of chromic anhydride amounted to 1 g per 100 ml in these determinations.

TABLE 3

Quantitative Determination of Thallium as Dichromate

Tl taken, in g	Tl found,* in g	Error, in mg
0.1000	0.0999	−0.1
0.0810	0.0810	0.0
0.0405	0.0405	0.0
0.0081	0.0080	−0.1
0.0040	0.0032	−0.8
0.0040**	0.0039	−0.1

*Mean values of several determinations.

**The precipitate of $Tl_2Cr_2O_7$ plus mother liquor were stood overnight; they were cooled again before filtration.

The results obtained show that when the thallium dichromate precipitate is less than about 0.01 g, it must be kept longer in contact with the mother liquor in order to ensure quantitative precipitation. Accordingly, it is necessary to leave precipitate and solution overnight and keep them cool, and then carry out the determination by the technique developed.

The new method suggested for the quantative determination of thallium as the dichromate has a number of advantages over its determination as the chromate. The main advantage of this method is the possibility of carrying out a direct determination of thallium without preliminary separation from metals which accompany it, in particular from those metals which form hydrated precipitates in alkaline solutions, and which, under the conditions used for the chromate method, require special methods for separating them.

Thallium chromate is precipitated quantitatively over a narrow concentration range of ammonia and potassium chromate [44]. It is possible, however, to vary the concentration of both acid and chromic anhydride over a wide range when thallium is precipitated as the dichromate.

Thallium dichromate separates out from solution more readily and more rapidly than the chromate; it separates out as a heavy, coarse precipitate which is readily filtered and washed. Precipitated thallium dichromate, in contrast to the chromate, need not be kept for such a long time in contact with the mother liquor in order to ensure quantitative precipitation (as long as the thallium concentration is not less than about 0.008 g).

The gravimetric method of determining thallium as the chromate can also be used in microdeterminations [45]. The results given in Table 3 give the basis for suggesting that determination of thallium as the dichromate could also be carried out by a quantitative microchemical analysis, as long as the appropriate conditions are used.

SUMMARY

1. A new method has been developed for the quantitative determination of thallium as the dichromate – $Tl_2Cr_2O_7$; this method is based on precipitation of thallium from neutral or acid solutions by means of chromic anhydride.

Optimum conditions have been established for determination of thallium as the dichromate by indirect volumetric and gravimetric methods.

2. The relation between the experimental error in determining thallium and the concentrations of sulfuric acid and chromic anhydride has been established. The limiting permissible concentrations of these two reagents for the quantitative determination of thallium have been determined.

3. It has been shown that thallium dichromate is an incongrously soluble and incongruously fusible compound.

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THE COLOR REACTIONS OF GALLIUM AND INDIUM SALTS WITH ORGANIC REAGENTS

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Comparatively few reactions are known for gallium and indium which can be used for developing photometric methods for determining these elements; accordingly, up to the present, only 8-hydroxyquinoline, quinalizarin, etc. [1] which have comparatively low specificity, have been used. The reactions of various hydroxyanthraquinones, and hydroxyquinones of the benzene and naphthalene series with indium salts have already been studied [2], nevertheless their characteristics and sensitivities were not discussed. The object of the work described here was the search for, and the study of, color (and fluorescent) reactions for gallium and indium.

Reactions with 2,2' Dihydroxyazo Dyes

o,o'-Dihydroxyazo dyes react with many metals to form compounds whose color differs from that of the reagent itself; in this connection therefore, they are used as indicators during titration with complexons. In the case of aluminum and gallium, the simultaneous appearance of an orange or red fluorescence with the change in color is characteristic. The analytical applicability and the composition of the compounds formed have been studied several times [3-6].

We have synthesized a number of representatives of this group of dyes, using 1-amino-2-naphthol-4-sulfonic acid and picramic acid as the first component of the azo compound, while phenols capable of supplying a hydroxyl group in the ortho position to the azo group on coupling were used as the second component.

The capacity of the synthesized dyes to react with gallium and indium salts at various pH values was studied, while the sensitivity of the reactions and their behavior toward Group III elements were also examined. In the course of this work it was established that some of these dyes give a fluorescent reaction with gallium salts which is more sensitive than those with dyes already known.

Table 1 contains details of the composition and formula of the dyes prepared, as well as the colors given by aluminum, gallium, and indium, and the sensitivity of the detection of gallium on the basis of observations of the orange-red illumination obtained on irradiating with an analytical quartz lamp. The reactions were carried out in the presence of buffer mixtures with a pH of 3-4.

As is evident from Table 1, the sensitivity of the detection of gallium with some of the newly synthesized compounds (No. 3, 4) is higher than with reagents which are already known (No. 1, 2). Reagent No. 3 is particularly suitable; the reaction with this reagent is carried on 2 ml of test solution in the presence of 2 ml of alcohol, a few drops of chloracetate buffer mixture* with a pH of 3.0, and a few drops of the dye solution (0.1% in alcohol being added. It should be pointed out that when gallium salts are used, the fluorescence is brighter in the presence of alcohol; in the case of aluminum salts a bright luminescence can be observed in the absence of alcohol, although in this case too, addition of alcohol enhances the intensity of the luminescence.

Dyes based on picramic acid either do not give a fluorescence or give a weak one; some of these dyes react with high sensitivity with gallium salts to give a variable color (Nos. 6, 8); it is characteristic that aluminum does not give a similar effect.

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*A mixture of equal volumes of 0.5 M monochloroacetic acid and its ammonium salt.

TABLE 1

Reactions of o,o'-Dihydroxyazo Dyes with Aluminum, Gallium, and Indium Salts

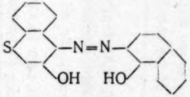
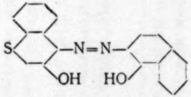
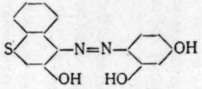
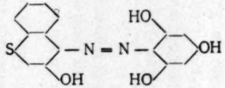
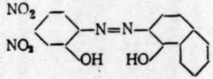
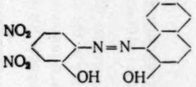
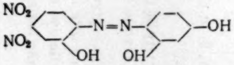
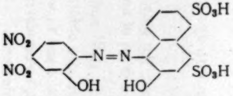
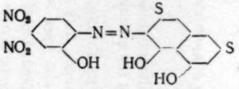
<table>
<tr><th rowspan="2">Expt. No.</th><th rowspan="2" colspan="2">Dye*</th><th colspan="4">Color of solution with dye and with salts</th><th rowspan="2">Sensitivity of gallium detection, in γ</th></tr>
<tr><th>Ga</th><th>Al</th><th>Zn</th><th>blank</th></tr>
<tr><td>1</td><td>4-Sulfo-2-hydroxynaphthalene-1-azo-2,1-hydroxynaphthalene</td><td> </td><td>Violet</td><td colspan="3">Red-violet</td><td>0,5</td></tr>
<tr><td>2</td><td>4-Sulfo-2-hydroxynaphthalene-1-azo-1,2-hydroxynaphthalene</td><td> </td><td>•</td><td>•</td><td></td><td></td><td>1,0</td></tr>
<tr><td>3</td><td>4-Sulfo-2-hydroxynaphthalene-1-azo-4-1,3-dihydroxybenzene</td><td> </td><td>Red</td><td>Red</td><td colspan="2">Dark-red</td><td>0,05—0,1</td></tr>
<tr><td>4</td><td>4-Sulfo-2-hydroxynaphthalene-1-azo-4-1,3,5-trihydroxybenzene</td><td> </td><td>Raspberry</td><td>Brown-yellow</td><td>Red</td><td>Yellow</td><td>0,2</td></tr>
<tr><td>5</td><td>1-Hydroxy-4,6-dinitrobenzene-2-azo-2,1-hydroxynaphthalene</td><td> </td><td colspan="4">Greyish-violet</td><td>—</td></tr>
</table>

TABLE 1 (continued)

Expt. No.	Dye*		Color of solution with dye and with salts				Sensitivity of gallium detection, in γ
			Ga	Al	Zn	blank	
6	1-Hydroxy-4,6-dinitrobenzene-2-azo-1,2-hydroxynaphthalene		Red	Yellow-rose			—
7	1-Hydroxy-4,6-dinitrobenzene-2-azo-4-1,3-dihydroxybenzene		Brownish-yellow				—
8	1-Hydroxy-4,6-dinitrobenzene-2-azo-1,2-hydroxynaphthalene-3,6-disulfonic acid		Raspberry	Red-yellow	Rose	Red-yellow	0,2
9	1-Hydroxy-4,6-dinitrobenzene-2-azo-2-1,8-dihydroxynaphthalene-3,6-disulfonic acid		Violet	Green-blue	Violet	Red-violet	—

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*S stands for the SO_3H group.

TABLE 2

Reactions of Various Compounds with Aluminum, Gallium, and Indium Salts

Compound	Medium in which reaction was carried out	Color and reaction sensitivity with salts of			
		Ga	Al	In	Blank
The azo dye from H acid and resorcinol	Weak hydrochloric acid	Rose $1-2\,\gamma$	Rose	Yellow	Yellow
p-Nitrobenzeneazopyrocathechol	Acetic acid	Red $1\,\gamma$	Yellow-orange	Yellow	Light-yellow
Schiff base from o-amino-2-naphthosulfonic acid and salicylaldehyde	Weak hydrochloric acid	Yellow $1\,\gamma$	Yellow	Colorless	Colorless
Schiff base from H-acid and salicylaldehyde	Weak hydrochloric acid	Yellow $1\,\gamma$	Yellow	Colorless	Colorless
Gallein	Ditto	Red violet $0.2\,\gamma$			Rose-yellow
Dihydroxyfluorescein	Acetic acid, pH 4.5	Raspberry $0.5\,\gamma$	Orange		Yellow
o-Hydroxyphenylfluorone	Acetic acid plus pyridine	Raspberry $1\,\gamma$	Rose-Yellow	Raspberry	Rose-yellow
Diphenylcarbazone	Hydrochloric acid plus pyridine	–	–	Violet $0.5\,\gamma$	Colorless

Of considerable interest is the reaction of aluminum with dye No. 9, in view of the very sharp color change from red-violet to blue-green.

Dyes No. 4 and 8 can be used for detecting indium; the sensitivity of the reaction with the first of these was found to be 1 γ of Zn in 2 ml of solution (on adding 3 drops of an acetate buffer with a pH of 4).

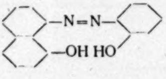
None of the elements tested – In, Mn, Ni, Co, Fe, Ti, Cr^{III} and Zn – give a similar illumination to gallium apart from aluminum. As for color changes, they are also obtained with many of the cations tested; thus, salts of Cr^{III}, Ni, Co, Ti, Zn and Fe^{II} react with dyes No. 4 and 6, while dye No. 8 reacts with salts of these metals as well as with those of chromium. Consequently, before carrying out reactions for gallium and indium, these elements should be separated from accompanying elements.

Of the synthesized reagents, 4-sulfo-2-hydroxynaphthalene-1-azo-1,3-dihydroxybenzene proved suitable for the quantitative determination of gallium in coal, ores, and industrial wastes with a sensitivity of some hundredths part of a percent [7].

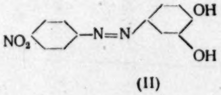
Reactions for Gallium and Indium with Some Other Compounds Containing Hydroxyl Groups

The reactivity of a series of colored organic compounds containing oxygen towards gallium, indium, and some other elements was studied; these compounds included:

1) Azo dyes containing two hydroxyl groups–one in the ortho and the other in the peri position (in the naphthalene series) with respect to the azo group (I).



(I)

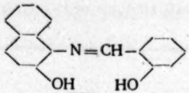


(II)

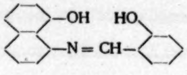
These dyes which are derivatives of diazotized "H" or "K" acids and resorcinol or orcin, are reagents for boric acid in weakly acid solutions [8].

2) An azo dye containing two hydroxyl groups in the ortho position with respect to each other, namely p-nitrobenzoazopyrocatechol (II). Derivatives of this type, as already established, are reactive toward germanium, zirconium, and gallium [9], and other elements.

3) Schiff Bases containing hydroxyl groups in the ortho (III) and peri positions (IV) with respect to the azomethine group



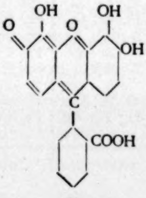
(III)



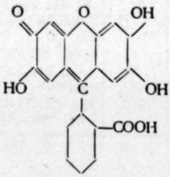
(IV)

In certain cases it is known that azomethine compounds of similar configuration react with the same elements as the corresponding azo dyes [10].

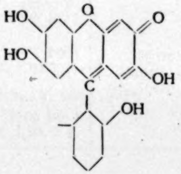
4) Dyes which are derivatives of fluorone—gallein (V), dihydroxyfluorescein (VI), and o-hydroxyphenyl-9-2,3,7-trihydroxy-6-fluorone (VII)



(V)

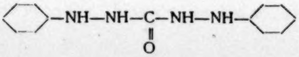


(VI)



(VII)

5) And, finally, a compound which does not belong to the group of dyes considered, namely diphenylcarbazone



The reactions of these compounds are given in Table 2.

As the results in Table 2 show, the compounds tested react mainly with gallium salts, only the last two react with indium. Although the sensitivity of the reactions is fairly high, the specificity is small; in addition to gallium, aluminum and some other elements also react with the first six compounds. For example, manganese, iron, and titanium salts react with the first dye, while iron and titanium salts react with the second.

Salts of trivalent iron (brown color) and zirconium (yellow precipitate with reagent No. 4) interfere with the reactions with the Schiff's bases. Iron, lead, bismuth, copper, tin, and zirconium salts interfere with reactions with the fluorone derivatives, while in the case of hydroxyphenylfluorone, zinc, nickel, and cobalt salts as well as other salts interfere in addition to salts of the elements already mentioned. Ferrous salts as well as indium salts interfere with diphenylcarbazone but ferric salts do not interfere, while nickel, cobalt, zinc, lead, and zirconium salts also interfere; salts of Al, Ti^{IV}, Cr^{III}, Mn, Bi, Cu, Cd, As^{III}, Sb and Sn^{IV} do not react.

All the same, despite their limited specificity, some of these reactions could be used under conditions where removal from accompanying elements is carried out prior to the photometric determination of indium or gallium; these dyes could also be used as indicators during the complexonometric titration of these elements. In particular, diphenylcarbazone is suitable for the determination of indium in germanium, the sensitivity in this case being of the order of some hundredths of a percent [11].

Color Reactions for Indium Based on Its Capacity to Form Complex Anions

The capacity of indium to form complex anions has been used to a comparatively small extent in analysis; it has only been used in certain microchemical reactions—with urotropine or quinoline [12], and with sparteine in the presence of thiocyanate [13]. The chemistry underlying these reactions consists of the formation of sparingly soluble salts of the organic bases with complex indium-thiocyanic acid. Formation of the indium iodide of methyl violet was suggested recently for the isolation of small amounts of indium by precipitation with organic coprecipitants [14].

TABLE 3

Reactions of Indium in the Form of a Complex Anion

Reagent	Added to the solution	Sensitivity, in γ, In	Behavior of other elements		
			do not react	give the same reaction	interfere
Rhodamine C	1 g KI; 1 *N* HCl, 4 drops	5	Ga, Al, Ti, Ni, Co, Zn, Sn	Cr, Mn, $Hg^{\cdot\cdot}$, Pb, Cd	Bi, Cu, Sb, Fe
	1 ml 40% KSCN	5	Al, Mn, Ni, Hg, As, Sb	Ga, Ti, Cr, Co,	Fe, Bi, Cu
Methyl violet	1 ml 50% KI; 1 *N* HCl, 2 drops	2	Ga, Al, Ti, Cr, Mn, Ni, Co, Zn, As, Sb^{III}, Sn^{IV}	Zn, Pb, Cd, Sn^{IV} Hg, Bi, Cd	Fe, Cu
•	1 ml 40% KSCN; 1 *N* HCl, 3 drops	0,2	Ga, Al, Ti, Cr, Mn, Ni, Pb, As, Sb, Sn^{IV}	Co, Zn, Hg, Cd	Fe, Cu

Since during the use of the basic organic dyes—methyl violet [15] and rhodamine C [16]—colored solid phase reactions may occur which can be used for determining many metals, we studied the suitability of these reagents for detecting indium by means of color reactions.

To 2 ml of a solution of an indium salt was added a halide (thiocyanate) of an alkali metal in sufficient amount to give a concentration of 13-50%, this was followed by the dye solution. Where necessary, the solution was acidified with a few drops of 1 N hydrochloric acid. The color obtained was compared with the color of a control solution.

Chloride, bromide, iodide, and thiocyanate were tried as complexing agents, but only iodide and thiocyanate proved suitable. When methyl violet was used, the color of the control was green, while the test solution containing indium had a violet color and a precipitate of the same color was formed; when rhodamine C was used, the control solution was of a pale-lilac color, almost colorless, while that of the test solution was violet.

Results of these reactions are given in Table 3.

As these results show, the reaction with iodide is more specific than that with thiocyanate. The specificity of the reaction for indium can be enhanced by using appropriate masking agents; thus, in the reaction with thiocyanate and rhodamine, zinc and cadmium can be masked by addition of potassium cyanide and pyridine.

SUMMARY

A study has been made of various color reactions given by certain organic compounds with gallium and indium; these compounds included o,o'-dihydroxyazo dyes, azo dyes containing hydroxy groups in other positions, and Schiff bases and phenylfluorone derivatives; a study has also been made of a number of reactions for indium based on the capacity of indium to form complex anions. It has been established that some of these compounds give more sensitive reactions with gallium and indium than representatives of this group which have been studied previously. Thus, gallium can be detected more sensitively by the fluorescence it gives with the dye 4-sulfo-2-hydroxynaphthalene-1-azo-1'-2,4-dihydroxybenzene; indium can be detected by means of a color reaction with diphenylcarbazone and by means of reactions with some other reagents. Results are given for the sensitivity and specificity of the reactions.

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[16] V. I. Kuznetsov, Proc. Acad. Sci. USSR 52, 231 (1946).

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*In Russian.

** [8] omitted in the Russian — Publisher's note.

***Original Russian pagination. See C. B. Translation.

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DETERMINATION OF DI- AND TRIVALENT TITANIUM IN SLAGS CONTAINING METALLIC AND DIVALENT IRON

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In the first communication [1] a method was described for the determination of total lower oxides of titanium in slags containing divalent iron. The method consists essentially of decomposing the slag in acid in the presence of salts of quinquevalent vanadium and trivalent iron, which oxidize the di- and trivalent titanium, and the divalent iron present.

Excess of oxidizing agent is titrated with a solution of Mohr's salt. Divalent iron is determined on a separate aliquot. The next stage which we undertook was the development of a method for the separate determination of di- and trivalent titanium in slags containing metallic and divalent iron.

When an aliquot of slag is decomposed in orthophosphoric acid on heating in an atmosphere of carbon dioxide, divalent titanium is oxidized to the trivalent state which is stable under these conditions. During the decomposition of an aliquot of slag in a mixture of HF + H_2SO_4 in the presence of excess of a solution of ferric ammonium alum, divalent iron is formed in an amount which is equivalent to the total di- and trivalent titanium present.

In order to check on the stability of trivalent titanium on heating in a solution of orthophosphoric acid, parallel determinations of trivalent titanium in slags were carried out by dissolving aliquots in orthophosphoric acid.

TABLE 1

Reproducibility of Determinations of Ti_2O_3 in Slags (in %)

Sample No.	Parallel determinations	Mean
2412	12,50; 12,75; 12,50; 12,78	12,63±0,13
2405	18,11; 18,27; 18,12; 18,47; 18,24	18,24±0,10
2406	20,57; 20,95; 20,94; 20,24; 20,42	20,62±0,26
2411	40,98; 41,07; 40,71; 40,27	40,76±0,27
Ti_2O_3 oxide	90,51; 92,60; 90,72; 91,62	91,36±0,75

As the results in Table 1 show, the parallel determinations show good reproducibility; the mean deviation does not exceed 1% (relative). When the content of trivalent titanium as determined by decomposition of an aliquot in orthophosphoric acid corresponds to its actual amount, then on summing the results of the determinations of all the components the total should not exceed 100%.

In order to confirm the correctness of this conclusion, some anosovites were analyzed and the trivalent titanium content also determined (Table 2).

From the results given in Table 2 it follows that only summation of the contents of Ti^{III} and Ti^{IV} permits

TABLE 2

Complete Analysis of Anosovites (in %)

Sample No.	Ti_2O_3 parallel determinations	Ti_2O_3 mean	SiO_2	Fe_2O_3	FeO	Fe_{metal}	TiO_2	Al_2O_3	MnO	MgO	CaO	Total I	TiO (Total titanium)	Total II
115	26,96; 27,30	27,13±0,17	3,07	—	2,33	—	53,03	6,20	0,60	8,13	—	100,49	83,17	103,50
119	28,34; 28,00	28,17±0,17	—	—	1,34	0,21	53,10	7,60	0,57	9,05	—	100,04	84,40	103,17
124	26,26; 25,92	26,09±0,17	3,20	—	2,99	—	54,40	5,65	0,58	6,97		99,88	83,38	102,77

one to get a total of 100% for full analysis of a sample. When the content of Ti^{III} is not taken into account, and titanium is determined as Ti^{IV}, the sum for complete analysis of an analysis is 2.8-3.5% greater than the normal sum (100%), and amounts to 102.77-103.5%. This difference will be larger the greater the Ti^{III} content of the sample. Thus, these results indirectly confirm that the trivalent titanium content established by dissolving the sample in orthophosphoric acid is the correct one.

In addition, Ti^{III} was determined in anosovites by two methods: by dissolving the sample in orthophosphoric acid, and in a mixture of hydrofluoric and sulfuric acids in the presence of excess ferric ammonium alum. When the Ti^{III} is not oxidized in the solution of orthophosphoric acid on warming, the results obtained by the two methods mentioned should coincide.

The results obtained are given in Table 3.

It follows from the results given in Table 3 that those obtained for the determination of trivalent titanium by dissolving the sample in orthophosphoric acid are in good agreement with those obtained by dissolving the sample in a mixture of hydrofluoric and sulfuric acids in the presence of ferric ammonium alum; they agree to an accuracy of 1% relative, this testifies to the stability of trivalent titanium in orthophosphoric acid on heating.

The last two columns in Table 3 contain the results for the increases in weight which were determined on heating a sample of slag to constant weight at 900° in a stream of oxygen, and the increases in weight calculated on the basis of the content of trivalent titanium, metallic and divalent iron.

The experimental and theoretical increases in weight are in good agreement; this confirms the reliability of the methods for determining trivalent titanium, metallic and divalent iron.

These results again confirm the stability of trivalent titanium in orthophosphoric acid on heating.

Divalent titanium is unstable in a solution of orthophosphoric acid, and is quantitatively oxidized to the trivalent state. Thus, during determination of divalent titanium by the two methods: dissolving an aliquot in orthophosphoric acid, and also dissolving an aliquot in a mixture of hydrofluoric and sulfuric acids in the presence of ferric ammonium alum, the following results were obtained (Table 4).

It follows from the results given in Table 4 that during titration of the solution obtained by decomposing the oxide by heating in orthophosphoric acid, the number of milliliters of standard solution used was only half of that used during titration of the solution obtained after decomposing an aliquot in a mixture of hydrofluoric and sulfuric acids in the presence of ferric ammonium alum. Actually, during dissolution of a sample in orthophosphoric acid, divalent titanium is oxidized to give an equivalent amount of trivalent titanium. Thus, the change $Ti^{II} \rightarrow Ti^{III}$ is not registered, and the number of milliliters used up in the titration only corresponds to the change $Ti^{II} \rightarrow Ti^{IV}$.

When an aliquot of test material is dissolved in a mixture of hydrofluoric and sulfuric acids in the presence of ferric ammonium

TABLE 3

Comparison of Results for the Determination of Trivalent Titanium by Two Methods

Sample No.	TiO_3			Fe metal	FeO	Increase in weight (experimental)	Increase in weight (calculated)
	sample dissolved in H_3PO_4	sample dissolved in HF + H_2SO_4 in the presence of alum	mean				
2407 Slag	23.88	24.21	24.04 ± 0.17	1.04	0.48	3.12	3.23
119 Slag	24.42	24.27	24.35 ± 0.08	1.53	2.33	3.89	3.89
119 Anosovite	28.17	28.15	28.16 ± 0.01	0.21	1.34	3.57	3.53
2411 Slag	40.76	39.78	40.27 ± 0.49	1.10	0.37	4.97	5.03

TABLE 4

Results of an Analysis of an Oxide Containing 89.30 TiO and 9.7 TiO_2 (in %)

Sample dissolved in H_3PO_4		Sample dissolved in a mixture of HF + + H_2SO_4 in the presence of alum	
milliliters of 0.1 N alum solution used for titration	mean	milliliters of 0.1 N $KMnO_4$ solution used for titration	mean
14.0; 14.1; 13.9	14.0 ± 0.10	28.0; 28.0; 27.8	27.9 ± 0.10

alum, divalent titanium is oxidized to the trivalent state, which, in turn, is further oxidized to quadrivalent titanium.

Accordingly, in this case, both the transition of Ti^{II} to Ti^{III} and of Ti^{III} to Ti^{IV} are registered, and the number of milliliters of titrant corresponds to the two stages of the oxidation of titanium.

Thus, as a basis of the method which has been developed for the separate determination of di- and trivalent titanium in slags, use has been made of the difference in the stability of titanium in these two valence states in a solution of orthophosphoric acid on heating. A description is given below of an analytical procedure for the determination of di- and trivalent titanium, and of metallic and divalent iron in slags.

1. Determination of trivalent titanium which represents total Ti^{III} present in the slag, and Ti^{II} oxidized to Ti^{III} during decomposition in orthophosphoric acid. 0.2-0.5 g of slag is placed in a 250 ml conical flask and 25-35 ml of orthophosphoric acid sp.gr. 1.7 added, a stream of carbon dioxide is then passed through the mixture for 15 minutes, and the sample decomposed by heating for 20-30 minutes with constant agitation. After decomposition is complete, the flask and the solution obtained is cooled and 50 ml of sulfuric acid 1 : 4 added, the solution is then cooled again to room temperature in a carbon dioxide atmosphere. The stream of carbon diozide is then switched off and 20 ml of a 40% aqueous solution of ammonium thiocyanate added, the solution is then titrated with 0.05 N ferric ammonium alum solution until the color of the solution changes from yellow to orange. Let the volume of ferric ammonium alum solution used for titration of total titanium (III) be denoted by V_1.

2. Determination of total Ti^{II} and Ti^{III} present in the slag. 0.2-0.5 g of slag is placed in a 100 ml conical flask and 15 ml of a 10% aqueous solution of $CuSO_4$ added, the mixture is diluted with distilled water to 50 ml and the whole boiled for 15-20 minutes in a stream of CO_2 in order to dissolve the metallic iron. Solution and precipitate are then filtered through a filter paper (red band) and the precipitate washed 4-5 times with hot water. Twenty ml of H_2SO_4 1 : 3 is added to the filtrate followed by 15 ml of H_3PO_4 sp.gr. 1.7, the total volume should be 150-200 ml; the solution is then titrated with 0.01 N ammonium vanadate using barium diphenylaminesulfonate as indicator, the color change being from light blue to blue; metallic iron is thereby

TABLE 5

Determination of TiO, Ti_2O_3, Metallic and Divalent Iron (in %)

Sample number	TiO		Ti_2O_3		F_{metal}		FeO	
	parallel determinations	mean	parallel determinations	mean	parallel determinations	mean	parallel determinations	mean
11 (Slag)	1,00; 0,92	0,96±0,04	12,27; 12,19	12,23±0,04	1,31; 1,25	1,28+0,03	2,00; 1,90	1,95±0,05
9 (Slag)	1,97; 1,87	1,92±0,05	12,88; 13,00	12,94±0,06	1,45; 1,34	1,39±0,05	1,99; 1,86	1,93+0,05
80 (Anosovite)	2,37; 2,10	2,24±0,13	56,27; 55,88	56,08±0,20	— —	—	— —	—
75 (Anosovite)	6,09; 5,42	5,75±0,34	55,28; 54,71	55,00±0,28	2,06; 2,08	2,03±0,04	0,70; 0,70	0,75+0,06
50 (Slag)	20,21; 20,53	20,37±0,16	2,63; 3,00	2,80±0,18	1,96		0,84	

determined. The filter paper and precipitate were treated with a hydrochloric acid solution of ferric chloride for 5 minutes in the cold in order to dissolve metallic copper. The precipitate is then transferred onto a filter paper (red band) and carefully washed with hot water, and then washed several times with cold 5% sulfuric acid. The precipitate is washed off the filter paper with a strong stream of hot water into a platinum basin 11 cm in diameter; excess ferric ammonium alum solution is then added, followed by 5 ml of sulfuric acid sp.gr. 1.84; the platinum basin is covered with another platinum basin 9 cm in diameter and a stream of carbon dioxide turned on for 15 minutes. Ten ml of hydrofluoric acid is then added, the total volume of the solution at this stage should be about 50 ml; the whole is thoroughly mixed and then heated for 20-30 minutes until the slag is completely dissolved. The solution is cooled in carbon dioxide stream and 20 ml of a saturated solution of boric acid added in order to complex the fluoride ions. The solution is transferred to a 500 ml flask containing 30-50 ml of distilled water, and 5 ml of sulfuric acid sp.gr. 1.84; divalent iron which is equivalent to total di- and trivalent titanium is then titrated with 0.05 N $KMnO_4$. Let the volume of $KMnO_4$ used for titration be denoted by V_2.

A correction must be applied to the titration result for the amount of divalent iron already present in the test material; in order to establish this correction, divalent iron should be determined on a separate aliquot by the following method.

0.5 g of slag is treated with cupric sulfate by the method described above in order to remove metallic iron. The slag is then decomposed in a platinum basin by heating with a mixture of 5 ml of sulfuric acid (sp.gr. 1.84), and 10 ml of hydrofluoric acid in an atmosphere of carbon dioxide, the total volume of the solution in the basin is made up to 50 ml with distilled water. When decomposition of the slag is complete the solution is transferred to a 500 ml flask containing 20 ml of a saturated solution of boric acid, 5 ml of sulfuric acid (sp.gr. 1.84), and 15 ml of orthophosphoric acid (sp.gr. 1.7); the total volume of the solution should be 150-200 ml. One ml of a 5% solution of sodium tungstate is added and residual, reduced titanium, which has not been completely oxidized during decomposition in hydrofluoric acid, titrated with a potassium permanganate solution until the blue color disappears [1]. Divalent iron is then titrated in the same solution with 0.01 N ammonium vanadate, using barium diphenylaminesulfonate as indicator.

Let the volume of ammonium vanadate used for titrating FeO present in the slag be denoted by V_3. The true volume of $KMnO_4$ used for titrating the divalent iron equivalent to total Ti^{II} and Ti^{III} is then given by the difference V_2-V_3, let this difference be denoted by V_0. The volumes of the standard solutions of ferric ammonium alum, potassium permanganate, and ammonium vanadate used for titration are reduced to unit weight and normality. Then (V_0-V_1) is the volume of standard solution which is equivalent to Ti^{II}, while $V_1 - (V_0 - V_1) = (2V_1 - V_0)$ is the volume of standard solution equivalent to Ti^{III}.

The percentage contents of TiO and Ti_2O_3 are calculated by means of the formulas:

$$\% \, TiO = \frac{63.9 \cdot N (V_0 - V_1)}{1000 \cdot n} 100,$$

$$\% \, Ti_2O_3 = \frac{143.8 \cdot V (2V_1 - V_0)}{2 \cdot 1000 \cdot n} 100,$$

where N is the normality of the standard solution and n is the weight of sample.

Blanks must be carried out.

Table 5 contains results for the determination of TiO, Ti_2O_3, metallic iron and divalent iron in slags and anosovites.

The results obtained are reproducible. The accuracy (mean deviation of duplicates) amounts to 0.5-1.0% (relative) for titanium contents of 10 to 60%, and to 6% (relative) for titanium contents of 1-5%; this is fully satisfactory for establishing in what form the titanium exists in the slags.

The author wishes to thank A. I. Ponomareva and B. N. Melent'eva for help and advice in preparing the article for the press.

SUMMARY

A method has been developed for the separate determination of di- and trivalent titanium in slags containing metallic and divalent iron.

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DETERMINATION OF URANIUM BY MEANS OF POTASSIUM IODATE

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Methods based on the formation of sparingly soluble compounds of quadrivalent uranium which are stable in mineral media are of considerable interest from an analytical point of view. The main drawback of such methods, however, is the complexity of the subsequent determination of uranium [1-5].

In the work described here which was carried out in 1952, the iodate method suggested earlier by Chernikhov and Uspenskii [6, 7] for the determination of thorium, zirconium, and cerium, was used for the direct determination of uranium. In the course of this work the optimum conditions for formation of a precipitate of the iodate of quadrivalent uranium with a definite composition were established, as well as the possibility of determining uranium gravimetrically and titrimetrically.

Preliminary tests showed that it is impossible to prepare a precipitate of constant composition when Kaufman's method is used [5]; according to this method, to a test solution containing 4-5% sulfuric acid by volume, an equal volume of 10% KIO_3 in 10% H_2SO_4 is added followed by twice the volume of 0.8% solution of KIO_3 in 2% H_2SO_4. It was found necessary to decrease the amount of 10% KIO_3 solution; thus, for contents of 5 mg and more of uranium, it was necessary to add it in the proportion of 1 : 2 to the volume of test solution takén, while in the presence of smaller amounts of uranium (1-2 mg) it was found necessary to add it in the proportion of 2 : 3 with respect to the test solution. The 0.8% solution of KIO_3 should be added, as indicated already, in an amount which is double that of the original volume of solution; this volume was 15-30 ml in all our tests. Quadrivalent uranium was prepared electrolytically on a mercury cathode [8].

The uranium iodate precipitate was filtered through a No. 4 glass crucible and washed with a dilute solution of potassium iodate (0.4% KIO_3 in 1% H_2SO_4) and then with alcohol and ether. The precipitate washed in this way readily came to constant weight at a temperature of 100-120°, and did not decompose on heating to 170°. It should be pointed out that when the precipitate was only washed with potassium iodate solution and alcohol, decomposition was observed as low as 60°.

The uranium content of the precipitate was determined by permanganatometric titration and by calcining to U_3O_8. Iodate was determined iodometrically after dissolving the precipitate in sulfuric acid and oxidizing the uranium with potassium permanganate to the sexivalent state.

The absence of potassium in the precipitate was established by a microcrystalloscopic reaction with chloroplatinate after decomposition of the precipitate and removal of uranium. On the basis of the weight of the precipitate and the uranium and iodate content which were determined experimentally, it was established that no water of crystallization is present in the precipitate dried at 110-120°.

The analytical results are presented in Table 1.

Accordingly, the composition of the precipitate of uranium iodate precipitated under the conditions outlined above, corresponds to the formula $U(IO_3)_4$. The conversion factor to uranium is 0.2539. It has been shown in this way that it is possible to determine uranium (IV) gravimetrically as its iodate. Table 2 contains results of determinations of various amounts of uranium.

Iodometric titration can be used for the titrimetric determination of uranium. For this purpose, the

TABLE 1

Results of the Analysis of Precipitated Uranium Iodate (calculated value of U for $U(IO_3)_4$, 25.39%; IO_3 content = 74.61%)

U found, in %	IO_3 found, in %
25.65	74.64
25.38	74.15
25.31	74.56
25.16	74.88
25.42	75.02
Mean 25.38	Mean 74.65

TABLE 2

Gravimetric Determination of Uranium as Iodate (mean of 3-4 determinations)

Uranium taken, in mg	Weight of precipitate, in mg	Uranium found, in mg	Error	
			in mg	in %
13.50	52.9	13.43	−0.07	−0.5
13.50	53.8	13.64	+ 0.14	+ 1.0
6.75	26.2	6.65	−0.10	−1.5
6.75	26.8	6.80	+ 0.05	+ 0.7
1.686	6.513•	1.654	−0.032	−1.9
1.686	6.661•	1.691	+ 0.005	+ 0.3
1.686	6.714•	1.704	+ 0.018	+ 1.1
			Mean	± 1.0

•Weighed on a microbalance.

TABLE 3

Titrimetric Determination of Uranium as Iodate

Uranium taken, in mg	$Na_2S_2O_3$ used up, in ml	Uranium found, in mg	Error	
			in mg	in %
6.750	12.40•	6.685	−0.065	−1.0
6.750	12.60•	6.790	+ 0.040	+ 0.6
3.375	6.30•	3.395	+ 0.020	+ 0.6
2.680	20.70••	2.692	+ 0.012	+ 0.4
2.680	20.50••	2.667	−0.013	−0.5
1.686	13.10••	1.704	+ 0.018	+ 1.0
1.686	12.85••	1.671	−0.015	−0.9
1.349	10.35••	1.346	−0.003	−0.2
1.349	10.40••	1.353	+ 0.004	+ 0.3
			Mean	± 0.6

•0.04981 N $Na_2S_2O_3$ used.

••0.01201N $Na_2S_2O_3$ used.

uranium iodate precipitate which had been precipitated and washed as indicated above, was dissolved in 20 ml of 10% sulfuric acid and 20 ml of 5% potassium iodide solution added, the liberated iodine was then titrated with thiosulfate. Special experiments showed that part of the iodine liberated reacts with quadrivalent uranium;

$U^{4+} + I_2 + 2H_2O = UO_2^{2+} + 2I^- + 4H^+$. Thus one atom of uranium corresponds to 22 gram equivalents of iodine.

Results of titrimetric determinations of uranium are given in Table 3.

Copper and molybdenum do not form iodates under the conditions used for precipitating uranium iodate; moreover, they can be removed by electrolysis on a mercury cathode.

TABLE 4

Titrimetric Determination of Uranium in the Presence of Aluminum

Ratio of U : Al	Taken, in mg		Uranium found, in mg	Error	
	aluminum	uranium		in mg	in %
1:10	70	6.745	6.734	−0.011	−0.16
1:10	14.2	1.349	1.358	+0.009	+0.66
1:50	330	6.745	6.675	−0.070	−1.3
1:50	72	1.349	1.387	+0.038	+2.7
1:75	550	6.745	6.419	−0.326	−4.8
1:100	660	6.745	6.088	−0.657	−9.5
1:100	135	1.349	1.165	−0.184	−14.0

Vanadium, which is reduced during the electrolysis process, is not precipitated either during precipitation of uranium iodate.

As the results in Table 4 show, aluminum present in amounts which are 50 times that of uranium, does not interfere. Nevertheless, when the amount of aluminum present is greater than this, appreciable losses of uranium are observed; this could be explained, presumably, by a salt effect.

Divalent iron, even at low concentrations, leads to incomplete precipitation of uranium. For example when the iron content is 0.5 mg, the experimental error is 10-15%. This phenomenon can be explained by the fact that the trivalent iron formed oxidizes iron to the sexivalent state.

SUMMARY

Conditions have been established for precipitating uranium as the iodate of quadrivalent uranium with a constant composition expressed by the formula $U(IO_3)_4$. It has been found that the iodate method can be used for both the titrimetric and gravimetric determination of uranium. The effect of certain elements on the accuracy of uranium determination has been studied. It has been found that it is possible to determine uranium in the presence of aluminum. Iron must be removed beforehand.

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THE SEPARATION OF URANIUM AND VANADIUM

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Many methods are known for the separation of uranium and vanadium [1-4], but several of them give incomplete separation, and require several reprecipitations. The disadvantage of the separation methods is particularly obvious in those cases where the reactions on which the separations are based are carried out in solutions which are almost neutral. The difficulty encountered in trying to separate these two elements suggest that there may be some interaction between uranium and vanadium. This possibility is indirectly confirmed by the existence of a number of natural minerals—uranovanadates—and by the ease with which uranovanadates can be synthesized from aqueous solutions under laboratory conditions.

In a previous paper [5] we showed that in aqueous solution, quinquevalent vanadium and sexivalent uranium form a complex uranovanadium anion. The acid corresponding to this anion, as well as the salts of the acid, are sparingly soluble in water, and are deposited from solution at a concentration as low as $5 \cdot 10^{-5}$ g-ion/liter, the composition of the precipitate formed varying with changes in the ratio of U : V in solution. When the solution contains excess uranium, the ratio U : V in the precipitate increases to 1.5 : 1; while, on the other hand, when vanadium is present in excess, this ratio decreases to 1 : 2 and less. We should like to point out that we analyzed the precipitates 24 hours after pouring together the appropriate solutions; this time interval was necessary for complete formation of the complex anions in solution.

The possibility of synthesizing compounds with a low ratio of U : V in the absence of a whole number value for the share of the vanadium, gave the basis for assuming that there occurs a gradual substitution of OH groups in the complex by metavanadate anions VO_3^- right up to the formation of a completely substituted uranyltrimetavanadate.

Depending on the ratio of uranium to vanadium in the solution one might expect that the precipitates formed will be a compound of one of the following three complex anions:

Uranyldihydroxymetavanadate $[UO_2(OH)_2VO_3]^-$

Uranylhydroxydimetavanadate $[UO_2(OH)(VO_3)_2]^-$

Uranyltrimetavanadate $[UO_2(VO_3)_3]^-$.

The composition of some natural minerals—the uranovanadates—is in good agreement with this assumption.

The formation of similar types of complex compounds undoubtedly may be a source of error in trying to carry out reactions for separating uranium and vanadium. Accordingly, in order to evaluate methods for the analytical separation of these elements, it is desirable to know the solubility of uranovanadates and the pH ranges within which they are stable.

The work described here was devoted to the study of these problems. In this connection, since it was impossible in practice to separate the free acids from the solutions in which they were formed, we confined ourselves to their ammonium salts during the solubility studies.

The effect of the composition of the solution, and the contact time of solution and precipitate, on the composition of the precipitate. In order to establish the effect of increasing the proportion of vanadium in solution, and of the total concentration of the reactants, on the composition of the precipitate, solutions with varying U : V ratios and different uranium concentrations were prepared. The solutions were placed in flasks which were tightly sealed with rubber stoppers well smeared with grease; the contact time between solution and the precipitate formed in it was varied for each solution.

The uranium and vanadium contents of the precipitates were determined photometrically by the peroxide method, after removing the precipitates from the solution by filtering them through No. 2 ultrafilters, and dissolving them in dilute sulfuric acid.

The results obtained (Table 1) show that increasing the vanadium concentration in solution to a value which is three times that of uranium slows down the formation of uranyltrimetavanadate. Even under favorable values of U : V, in solution however, formation of uranyltrimetavanadate proceeds slowly, and requires not less than three months for uranium concentrations in the original solution of $5 \cdot 10^{-4}$ g-atom/liter, and about 6 months when the initial uranium concentration of the solution is ten times as much.*

TABLE 1

Uranium taken, in g-atom/liter	Atomic ratio U : V					
	in the original solution	in the precipitate after standing for:				
		24 hours	10 days	one month	three months	six months
$5 \cdot 10^{-4}$	1 : 3	1 : 2.5	1 : 2.6	1 : 2.9	1 : 3	1 : 3
	1 : 5	1 : 2.5	1 : 2.6	1 : 2.7	1 : 2.9	1 : 3
$5 \cdot 10^{-3}$	1 : 3	1 : 2.5	1 : 2.7	1 : 2.8	1 : 2.9	1 : 3
	1 : 5	No precipitate	1 : 1.5	1 : 1.5	1 : 1.5	1 : 1.5

TABLE 2

Uranium Concentration of the Original Solution, in g-atom/liter $5 \cdot 10^{-4}$

Ratio U : V, in g-atom		
in the original solution	in the precipitate	
	after heating	in the cold
1 : 1	1 : 1	1 : 1
1 : 2	1 : 2	1 : 1.8
1 : 3	1 : 3	1 : 2.5
1 : 5	1 : 3	1 : 2.6

The experiments described were carried out at room temperature. We tried to increase the rate of formation of uranyltrimetavanadate by heating the solution containing uranium and vanadium. Qualitative observations showed that the precipitate is formed more rapidly under these conditions.

Table 2 contains results obtained during determination of the proportion of U : V in precipitates obtained on heating the solution to the boiling point (the precipitates were analyzed one hour after pouring the solutions together). For comparison, results are given for precipitates obtained under similar conditions at room temperature (the analysis was carried out 24 hours after pouring the original solutions together).

It is obvious that heating accelerates formation of the end product of the substitution of OH^- by VO_3^- in the complex uranovanadium anion.

The reason for this speeding up could be either an increase in the solubility of the uranylvanadate containing the least vanadium, or a weakening of the U – OH bond with increasing temperature. It is possible, of course, that both factors operate at once.

*This is connected with polymerization of vanadate [2] at such high concentrations. The monoform of metavanadic acid enters into the composition of the complex. The appearance of polymers lowers its concentration, and initially slows down (c_V about $n \cdot 10^{-3}$ g-atom/liter), and then prevents formation of the trimetavanadate (c_V about $2.5 \cdot 10^{-2}$ g-atom/liter).

TABLE 3

Ratio of U:V in the original solution		Concentration of acid or alkali					(Normality)*				
		HCl					NaOH				
		10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
1:1	pH solution	3.1	3.0	2.8	2.1	1.1	3.2	3.4	4.0	4.9	6.4
	U:V in the precipitate	1:1.1	1:1.15	1:1	1:1.1	No precipitate	1:1.1	1:1	1:1.15	1:1	No precipitate
1:2	pH solution	3.3	2.9	2.8	2.3	1.4	3.3	3.5	4.1	5.0	6.6
	U:V in the precipitate	1:1.9	1:1.89	1:1.9	1:1.85	No precipitate	1:1.9	1:1.9	1:1.9	1:1.9	No precipitate
1:3	pH solution	3.3	3.3	3.3	2.8	2.2	3.7	3.9	4.2	5.8	6.7
	U:V in the precipitate	1:2.6	1:2.5	1:2.5	1:2.5	No precipitate	1:2.5	1:2.5	1:2.5	1:2.6	No precipitate
1:5	pH solution	4.3	4.3	4.1	3.2	2.1	3.74	4.5	5.4	5.6	6.7
	U:V in the precipitate	1:2.8	1:2.8	1:2.8	1:2.8	No precipitate	1:2.8	1:2.8	1:2.8	1:2.8	No precipitate

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*The normality indicated here would be that obtained when the alkali (acid) is added to distilled water. The true concentration of free H^+ ions in the solution over the precipitate is expressed by the pH values.

TABLE 4

Percentage content			Total percent	Molecular ratio
U_3O_8	V_2O_5	Loss on calcination		$U_3O_8 : V_2O_5 : H_2O$
68.1	22.2	9.8	100.0	1 : 1.5 : 6.1
54.4	34.2	11.3	100.6	1 : 3 : 9
44.7	42.4	12.6	99.7	1 : 4.5 : 12.1

TABLE 5

Percentage content					Molecular ratio
U_3O_8	V_2O_5	Loss on calcination	NH_3	H_2O	$U_3O_8 : U_2O_5 : NH_3 : H_2O$
68.2	22.1	9.61	4.1	5.4	1 : 1.5 : 3 : 3.5
53.5	34.6	11.86	3.17	8.7	1 : 3 : 3 : 7.6
44.3	42.4	13.5	2.9	10.5	1 : 4.5 : 3 : 11.1

TABLE 6

Time of agitation, in hours	Uranium concentration in the solvent, in μg/ml		
	I	II	III
1	0.096	0.041	0.024
2	0.110	0.042	0.023
3	0.100	0.041	0.023
4	0.100	–	–
Molar solubility (on an uranium basis)	$4.2 \cdot 10^{-7}$	$1.7 \cdot 10^{-7}$	$9.7 \cdot 10^{-8}$
Lp	$1.7 \cdot 10^{-13}$	$2.9 \cdot 10^{-14}$	$9.6 \cdot 10^{-15}$

The change in the composition of the uranylvanadates is related to changes in the amount of OH in the complex. It could be postulated that the composition of these compounds should depend on the pH of the medium. Table 3 contains the results of a series of experiments on the precipitation of uranylvanadates from solutions with a constant uranium concentration ($5 \cdot 10^{-4}$ g-atom U/liter) and variable vanadium concentration, when the pH of the solution was varied. The precipitates were analyzed 24 hours after pouring the solutions together.

From these results it is clear that precipitates are formed within the wide pH limits of 2.2-6.5; under these conditions their composition does not depend on the hydrogen ion concentration.

Precipitates which had separated out on heating solutions containing only uranyl nitrate and ammonium vanadate were also analyzed, as well as precipitates formed on heating solutions containing ammonium chloride as well as uranyl nitrate and ammonium vanadate. In the first instance solutions with ratios of uranium to vanadium of 1 : 1, 1 : 2, and 2 : 1 were prepared. After heating the solutions to the boiling point, the precipitates were filtered through a No. 2 ultrafiltrate, and washed with weakly acidified water, they were then dried at 102° in a thermostat and analyzed. The mean results of five determinations are given in Table 4.

On the basis of the analyses the formulas of these compounds were calculated:

1. $2UO_3 \cdot V_2O_5 \cdot 6H_2O$ or $H[UO_2(OH)_2VO_3]H_2O$
2. $UO_3 \cdot V_2O_5 \cdot 3H_2O$ or $H[UO_2(OH)(VO_3)_2]2H_2O$
3. $2UO_3 \cdot 3V_2O_5 \cdot 8H_2O$ or $H[UO_2(VO_3)_3]4H_2O$.

The precipitates contained a small amount of ammonia ($< 0.8\%$); it is possible that hydrogen was partially replaced by ammonium ions.

In a similar way compounds were synthesized in the presence of ammonium chloride, the concentration of the latter being 10^{-2} N. Results of the analyses of these compounds are given in Table 5. The following compounds were prepared in this way;

1. $2UO_3 \cdot V_2O_5 \cdot 2NH_3 \cdot 2.2H_2O$ or $NH_4[UO_2(OH)_2VO_3]$
2. $UO_3 \cdot V_2O_5 \cdot NH_3 \cdot 2.2H_2O$ or $NH_4[UO_2(OH)(VO_3)_2] \cdot 1.5H_2O$
3. $2UO_2 \cdot 3V_2O_5 \cdot 2NH_3 \cdot 7H_2O$ or $NH_4[UO_2(VO_3)_3] \cdot 3.5H_2O$.

Solubility of ammonium uranylvanadates. The solubility of the following three ammonium uranylvanadates: $NH_4[UO_2(OH)_2VO_3]$ (I); $NH_4[UO_2(OH)(VO_3)_2] \cdot 1.5H_2O$ (II); $NH_4[UO_2(VO_3)_3] \cdot 3.5H_2O$ (III), was determined in water and in aqueous solutions of ammonium chloride and hydrochloric acid at 18 and 50°.

The solubility determinations were made on the basis of uranium whose concentration was determined by the luminescent bead method according to Bykova's technique [6], using a LIuF-51 photometer.

The solubility was studied isothermally; the temperature was kept constant by means of a contact thermometer with an accuracy of ± 0.02° at 18°, and ± 0.1° at 50°. The test salt was placed in a vessel with a mercury seal and a screw-shaped stirrer connected to an electric motor. The stirring rate was 600-700 revolutions per minute. Fifty ml of solvent was introduced into the vessel.

TABLE 7

Time of agitation, in hours	Uranium concentration in solution, in μg/ml					
	18°			50°		
	I	II	III	I	II	III
1	0.065	0.008	0.016	0.12	0.069	0.040
2	0.100	0.013	0.032	0.15	0.071	0.041
3	0.150	0.050	0.038	0.15	0.069	0.041
4	0.180	0.069	0.037	0.16	0.070	0.040
5	0.180	0.070	0.037	–	0.071	–
6	0.180	0.070	0.038	–	–	–
Molar solubility (based on uranium)	$7.5 \cdot 10^{-7}$	$3.0 \cdot 10^{-7}$	$1.6 \cdot 10^{-7}$	$6.5 \cdot 10^{-7}$	$3.0 \cdot 10^{-7}$	$1.7 \cdot 10^{-7}$
Lp	$5.5 \cdot 10^{-13}$	$9.0 \cdot 10^{-14}$	$2.6 \cdot 10^{-14}$	$4.2 \cdot 10^{-13}$	$9.0 \cdot 10^{-14}$	$2.8 \cdot 10^{-14}$

Samples of solution were taken every hour; the aliquot was filtered through a No. 3 filter crucible, the filtrate was sucked off on a Komovskii pump. All these operations were carried out at constant temperature.

Table 6 contains the results obtained for the solubility of ammonium uranylvanadates in water at 18°, while Table 7 contains the results for the solubility in a 10^{-2} solution of ammonium chloride at 18 and 50°.

As these results show, the solubilities of the ammonium uranylvanadates in water and in dilute aqueous solutions of ammonium chloride are very similar and hardly change at all with temperature over the range 18-50°. This shows that the reason for the speeding up of the formation of the uranyltrimetavanadate on heating is connected with the greater stability of the bond U – VO_3 as compared with U – OH. The latter is

TABLE 8

Time of agitation, in hours	Uranium concentration in the solvent, in μg/ml			
	10^{-4} N HCl			10^{-3} N HCl
	I	II	III	I
1	0.146	0.058	0.033	0.10
2	0.225	0.121	0.071	0.25
3	0.267	0.120	0.076	0.51
4	–	0.120	0.077	0.60
5	–	0.120	0.077	0.62
6	0.265	–	–	0.62
7	–	–	–	–
8	–	–	–	–
9	0.266			
Molar solubility (based on uranium)	$1.1 \cdot 10^{-6}$	$5.0 \cdot 10^{-7}$	$3.2 \cdot 10^{-7}$	$2.5 \cdot 10^{-5}$
Lp	$1.2 \cdot 10^{-12}$	$2.5 \cdot 10^{-13}$	$1.0 \cdot 10^{-13}$	$6.2 \cdot 10^{-10}$

weakened on heating and accelerates the substitution of OH ions by VO_3^-. Determination of solubility at higher temperatures was complicated by the fact that the finely dispersed precipitates could not be removed from the hot solution by means of a filter even when a No. 4 filter crucible was used.

Table 8 contains the results of the solubility of the same salts in hydrochloric acid at 18°.

It is clear from this Table that the solubility of the salts in 10^{-4} N HCl is somewhat greater than in NH_4Cl solution. Increasing the acid concentration to 10^{-3} N increased the solubility even more, as was to be expected. Addition of acid affects the secondary dissociation of the salt according to the scheme

$$[UO_2(OH)_2VO_3]^- \rightleftharpoons UO_2(OH)_2 + VO_3^-,$$

the equilibrium state of which is strongly dependent on the pH of the solution since the pH determines the state of the uranyl and vanadium ions [5].

DISCUSSION OF RESULTS

The results obtained testify to the very low solubility of ammonium uranylvanadates (of the order of the solubility of the silver halides), this solubility decreasing in the sequence $NH_4[VO_2 \cdot (OH)_2VO_3] \rightarrow NH_4[UO_2(VO_3)_3]$. The solubility of the salts of these acids with divalent metals is, apparently, of the same order ($L_pBa[UO_2(OH)_2 \cdot \cdot VO_3]_2 \sim 10^{-21}$). The low solubility of the uranylvanadates which leads to coprecipitation of vanadium during the precipitation of various uranium compounds, is particularly clearly manifested in those cases where separations are carried out at a pH of 2.2-7.

The results we have obtained give a basis for postulating that separation of uranium and vanadium should be most complete in strongly acid or in strongly alkali solutions. Thus, under optimum conditions, separation can be effected by means of cupferron. The phosphate separation is less successful, since this method involves addition of a large amount of salts to the solution, and this facilitates deposition of uranovanadates in the precipitate; the hydrogen ion concentration in solution during all the separation operations is very close to that which is used for the interaction of uranium and vanadium. Furthermore, the solubility of the uranyl phosphates in ammonium chloride solutions is almost one order higher than that of ammonium uranyltrivanadate—the salt which is most probably formed during separation of uranium from excess vanadium. The addition of excess ammonium phosphate, and the alkalinification of the solution shifts the equilibrium according to the law of mass-action toward the formation of phosphates, and, in this way, favors the separation of uranium and vanadium.

Thus, separation of uranium (VI) and vanadium (V) in neutral and weakly acid media is not reliable. During their separation, one should presumably avoid long standing of weakly acid or neutral solutions containing these ions, particularly in the presence of "neutral" salts. It should also be remembered that heating strongly accelerates complex formation, and the formation of precipitates.

Where it is necessary to separate uranium from large amounts of the alkali and alkaline-earth metals, it is possible to use the low solubility of the uraniumvanadate salts of the chosen cation; this technique is especially useful for the isolation of small amounts of uranium from very dilute solutions. It is sufficient to add a 1-3 fold excess of ammonium vanadate to such a solution, and then acidify the solution (to pH 3.5-7) and finally heat to the boil.

SUMMARY

1. It has been found that the uranovanadic acids are precipitated at a pH of 2.2-6.5. Within these pH limits the composition of the precipitate is independent of hydrogen ion concentration.

2. It has been shown that the formation of ammonium uranyltrimetavanadate is a long process. At uranium concentrations of $5 \cdot 10^{-4}$ g·atom/liter, and a three fold excess of vanadium, it takes as long as three months at room temperature, while in the presence of a five-fold excess of vanadium the process takes six months. Heating the solution to the boil sharply increases the rate of formation of uranyltrimetavanadate.

3. The solubility of ammonium uranyldihydroxymetavanadate, uranlyhydroxydimetavanadate, and uranyltrivanadate has been determined.

4. Conditions have been established by means of which it should be possible to achieve the most complete separation of uranium (VI) and vanadium (V).

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SPECTROCHEMICAL DETERMINATION OF TANTALUM IN ZIRCONIUM

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Determination of small amounts of tantalum (< 0.01%) in zirconium is accompanied by a number of difficulties. Photometric methods of determining tantalum are not really suitable because of their relatively low sensitivity (40 γ in 20 ml). Further, during the photometric determination of tantalum by means of pyrogallic acid [1] titanium interferes to a considerable extent. The sensitivity of direct spectrographic determination of tantalum in zirconium is also low, and, according to our studies, amounts to $1 \cdot 10^{-2}$ %. The sensitivity of the spectrographic determination of tantalum can be increased by separating it beforehand from zirconium, the best method for separation being extraction of tantalum in the form of a fluoride complex [2-4]. For separating tantalum from titanium, Chernikhov, Tramm, and Pevzner [5] used extraction of the fluoride compounds with cyclohexanone (sp. gr. 0.95, b. p. 156°).

Our experiments have shown that extraction with cyclohexanone permits quantitative separation of tantalum from zirconium, while the small amounts of tantalum in the extract can be reliably determined spectrographically.

Separation of tantalum from zirconium by extraction with cyclohexanone. A standard tantalum solution (containing 0.5 mg of tantalum / ml) was prepared by fusing 0.0611 g of tantalum pentoxide with potassium pyrosulfate. The melt was dissolved in 2 M sulfuric acid containing 1-1.5 ml of hydrofluoric acid, the solution being made up to 100 ml with 2 M sulfuric acid.

Tantalum was extracted from 2-4 M sulfuric acid with cyclohexanone; three extractions were sufficient for the quantitative extraction of tantalum into the organic phase for a ratio of 1 : 1 for the aqueous and organic phases (Tables 1 and 2).

Experiments on the separation of comparatively large amounts of tantalum from zirconium (Table 3) showed that, under the conditions chosen, tantalum passes over completely into the organic phase, while almost all the zirconium remains in the aqueous solution.

For the spectrographic determination of small amounts of tantalum in the extract, it is sufficient to concentrate the tantalum solution to a small volume (2-3 ml) to ensure a high sensitivity. For this purpose it was found most convenient to distil the cyclohexanone as an azeotrope with water boiling at 90°; by using this technique, resinification of cyclohexanone is avoided.

The fact that no tantalum was lost during extraction and azeotropic distillation was established by using the radioactive isotope Ta^{182} (Table 4).

Choice of conditions for the spectrographic determination of tantalum in solution. For the spectrographic determination of impurities in small volumes of solution, the technique involving preliminary deposition and drying of the solution on the front of the electrode surface is widely used. The thin layer of deposit thereby obtained is then ignited in a spark or arc discharge.

Our experiments showed that the highest sensitivity is achieved during spark excitation of the spectrum and by using carbon electrodes 3-3.5 mm in diameter. Using these conditions, the sensitivity is approximately three times the sensitivity achieved by means of carbon electrodes of normal diameter (6 mm); when the ISP-22 spectrograph is used, this sensitivity amounts to 0.1 γ .

TABLE 1

Extraction of Tantalum by Means of Cyclohexanone at Various Sulfuric Acid Concentrations (1.0 mg of Ta taken)

H_2SO_4 concentration, in M	Ta determined, in mg	Error, in mg	Number of extractions
2	0.95	−0.05	3
2	1.00	0.0	4
3	1.04	+0.04	3
4	1.00	0.0	4
4	1.07	+0.07	4

TABLE 2

Amount of Tantalum in the Various Fractions During Extraction with Cyclohexanone

Tantalum taken, in mg	Tantalum extracted, in mg				Error, in mg
	fractions				
	I	II	III	total	
1	0.8	0.25	0.05	1.1	+0.1
1	0.85	0.10	0.05	1.0	0.0
2	1.6	0.25	0.075	1.93	−0.07

TABLE 3

Separation of Tantalum from Zirconium by Extraction with Cyclohexanone (100 mg Zr taken)

Tantalum taken, in mg	Amount detected in the extract, in mg	
	zirconium*	tantalum
1.0	0.014	1.0
1.0	0.016	0.95
2.0	0.07	2.0
2.0	0.023	2.0
1.0	0.011	1.0

---

*Zirconium was determined photometrically in the extract using arsenazo [6].

TABLE 4

Behavior of Tantalum During Extraction (Ta^{182} with 2420 impulses/minute taken)

Determination of tantalum, in impulses/minute				
in the rejected acid solution	in the organic phase after distillation	in the aqueous layer after distillation	in the main solution	total
3	—	9	2390	2402
5	3	11	2370	2389
8	—	20	2300	2328
—	8	6	2480	2494

TABLE 5

Passage of Tantalum into the Discharge as a Function of the Time of Spark Burning

Duration of spark discharge, in seconds	Intensity of the analytical line Ta 2685.1 A*		Amount of Ta^{182} on the electrodes, in impulses/minute*	
	electrode size, in mm			
	3	6	3	6
0	—	—	2820	2855
10	32.6	10.9	1012	1940
30	13.2	7.81	533	1241
50	6.00	6.50	290	947
70	2.54	5.75	176	693
90	—	4.80	84	517
110	—	3.53	—	349
130	—	2.11	—	270

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*Mean of three measurements.

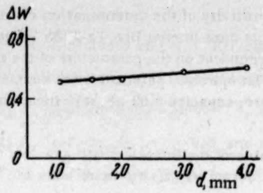

Fig. 1. Effect of the interelectrode gap on the valve of W.

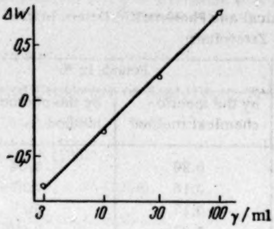

Fig. 2. Calibration curve.

TABLE 6

Effect of Acid Concentration on Tantalum Determination

H_2SO_4 concentration, in %	Ta introduced, γ/ml	Ta found, in γ/ml*
5	50	46
10	50	53
20	50	52
40	50	57

---

*Mean of three measurements.

TABLE 7

Effect of Zirconium on Tantalum Determination

Zr content, in γ/ml	Ta introduced, in γ/ml	Ta found, in γ/ml *
0	10	10.0
5	10	9.5
10	10	9.5
20	10	9.4
30	10	9.8

---

*Mean of six measurements.

TABLE 8

Results for the Spectrographic Determination of Tantalum in Zirconium

Ta introduced, in γ/ml	Ta found, in γ/ml*	Relative error, in %
14	14	0
16	11	21
20	26	30
20	20	0
7.5	8.0	7
7.5	9.0	20
10	12	20
10	14	40
25	24	4
25	21	16
16	16	0
16	18	12
12	8.0	33
16	11	31
16	12	25
12	11	8
15	13	13
15	14	7

---

*Mean of three measurements.

Studies of the "burning off" of the tantalum from the electrodes by means of a moving photographic plate, and also by means of radioactive Ta^{182}, showed that the increase in sensitivity in the case of a 3 mm electrode is the result of a more rapid passage of the tantalum into the discharge (Table 5). When the 3 mm electrodes were used, the main part of the tantalum passed into the discharge in the course of 40-50 seconds, while when 6 mm electrodes were used, the time taken was 100-120 seconds. Since the exposure time for registration of the spectra on "Type II" plates amounts to 20 seconds (any further increases in exposure time

TABLE 9

Spectrochemical and Photometric Determination of Tantalum in Zirconium

Sample No.	Found, in %	
	by the spectrochemical method	by the photometric method
1	0.26	0.24
2	0.16	0.17
3	0.17	0.17
4	0.035	0.035

lead to a significant increase in the background), the increase in sensitivity observed in the case of 3 mm electrodes is readily comprehended.

The sensitivity of the determination of tantalum by means of its most intense line Ta 2685.1 A is also essentially dependent on the parameters of the spark generator. The optimum parameters for the spark generator IG-2 are: capacity 0.02 μF, self-inductance 0.01 μH.

The value of the interelectrode gap does not show any strong effect on sensitivity; in our case this was 2 mm.

In order to increase the accuracy of the determination of tantalum in the extract, an internal standard was used, this was molybdenum, which was added to the test materials and to the standards in an amount of 15 γ/ml. The line Mo 2688.0 A served as a reference line. The analytical pair of lines Ta 2685.1 A / Mo 2688.0 A, as our experiments showed, is fully suitable for quantitative determinations. Changes in the interelectrode gap have almost no effect on the blackening difference (Fig. 1).

Standard solutions containing 3, 10, 30, and 100 γ of Ta/ml were prepared from a stock solution with a concentration of 0.5 mg/ml. Appropriate aliquots of the stock solution were transferred to 25 ml standard flask to which molybdenum was then added at the rate of 15 γ/ml, and the volume made up to the mark with water.

The calibration curve (Fig. 2) is best constructed within the coordinates logarithm c, ΔW (W is the transformed blackening), Within these coordinates, the curve is linear over the range 3-100 γ/ml Ta. Treatment of 15 photographic plates showed that the curves obtained for different plates are only insignificantly displaced parallel to one another. This indicates that it should be possible to use the method of a control standard when the conditions for exciting the spectra and treating the plates are strictly observed.

During extraction of tantalum, insignificant amounts of sulfuric acid (5-10%) and zirconium (Table 3) also pass into the organic phase. Accordingly, it was necessary to investigate the possible effect of the acidity of the concentrate, and the amount of zirconium in it, on the spectrographic results.

Determination of tantalum in solutions whose sulfuric acid content varied from 5 to 40%, showed (Table 6) that the acidity has almost no effect on the accuracy of the spectrographic analysis. All the same, the sensitivity of the determination is somewhat lower (approximately half as much for a 50% sulfuric acid content).

Similarily, zirconium contents of up to 30 γ/ml have no effect on tantalum determination (see Table 7).

The method developed for the spectrographic determination of tantalum in zirconium was used for the analysis of a series of zirconium samples to which known amounts of tantalum had been added (Table 8).

Determination of various concentrations of tantalum in zirconium by spectrochemical and photometric methods gave results which were in satisfactory agreement with each other (Table 9).

On the basis of the results given in Table 8, the accuracy of the method was evaluated as 20% (mean arithmetic error). The sensitivity of the spectrographic method of determining tantalum in sulfuric acid solution amounts to 3 γ/ml when two drops of the solution are placed on the electrodes. Accordingly, when 1 g of zirconium is taken and the extract obtained is evaporated to 2-3 ml, it is possible to determine about $1 \cdot 10^{-3}$ % of tantalum in the zirconium. The sensitivity can be increased by increasing the weight of the aliquot taken and by evaporating the extract to a smaller volume.

The authors wish to thank L. V. Lipis for valuable advice and for his continued interest in the work.

SUMMARY

A spectrochemical method is suggested for the determination of small amounts (< 0.01%) of tantalum in zirconium; the method is based on the separation of tantalum from zirconium by extraction of the fluoride complex of tantalum from a sulfuric acid medium by means of cyclohexanone; this is followed by spectrographic determination of tantalum in the extract after removal of the cyclohexanone as an azeotropic mixture with water. Molybdenum is used as an internal standard.

The method permits determination of down to $1 \cdot 10^{-3}$% of tantalum in 1 g of zirconium with a mean arithmetic error of about 20% relative.

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DETERMINATION OF CALCIUM, MAGNESIUM, ALUMINUM, SILICON, AND TIN IN REFINED PLATINUM AND PALLADIUM

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Spectrographic determination of small amounts of Ca, Mg, Al, Si, and Sn in refined platinum and palladium is best carried out in solution, since the preparation of standards in the form of melts is a difficult problem, while standard powders do not guarantee the requisite accuracy in the case being discussed. During work with solutions we adopted the technique described by S. A. Borovik and T. F. Borovik-Romanova [1].

Using water twice distilled in quartz vessels and acidified with distilled hydrochloric acid, a number of solutions were prepared from analyzed, chemically pure spectroscopic quality $CaSO_4$, $Mg(NH_4)_2$, $(SO_4)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $SnCl_2 \cdot 2H_2O$; the solutions prepared contained Ca, Mg, Al, Si, and Sn in amounts ranging from $3 \cdot 10^{-6}$ to $1 \cdot 10^{-2}$%. The solution of sodium silicate was prepared by dissolving a melt of chemically pure silica and sodium carbonate in water; the silicon concentration of the solution obtained was determined chemically.

The solutions were placed successively in a sprayer, into which fresh solution was fed every minute during the course of the experiment. An a.c. arc was used. The spectra were photographed on a Hilger spectrograph (the average model) using NIKFI (Type 2) plates.

The following pairs of lines were used for constructing calibration curves.

Ca II – 3933.67 – Pt I 3966.36
Mg II – 2802.7 – Pt I 2803.24
Al I – 3961.52 – Pt I 3966.36
Si I – 2881.58 – Pt I 2893.87
Sn I – 3034.12 – Pt I 3036.43

The internal standard used was the background in the neighborhood of the line being photographed [2]. Scattering of the points was insignificant over the concentration range $3 \cdot 10^{-6}$ to $1 \cdot 10^{-2}$%. A solution containing 1% of platinum was then prepared, the platinum compound used was platinum cis-dinitrodichlorodiammine – $(NH_3NO_2)_2Cl_2Pt$ (Blomstrand's salt); this salt was recrystallized twice, nevertheless small amounts of calcium could still be detected in it, and this could not be removed despite several recrystallizations. Accordingly, corrections were applied to the results obtained, for the amount of this impurity; this was determined by extrapolation.

Standard solutions with concentrations of 0.0001 – 0.01% of Ca, Mg, Al, Si, and Sn were prepared by pouring together the solution which is 1% with respect to platinum and appropriate amounts of 0.0002, 0.0006, 0.002, 0.006, and 0.02% solutions of the salts of the impurities being determined. The solutions prepared in this way contained 0.5% Pt and 0.0001, 0.0003, 0.001, 0.003, and 0.01% of the impurities being determined.

The calibration curves prepared (Fig. 1) permitted determination of down to 0.002% of Ca, down to 0.02% of Mg, 0.02% of Al and Si, and 0.06% Sn. The mean error for the determination of calcium, magnesium, and aluminum was ±6%, while the error for determination of silicon and tin was ±9%.

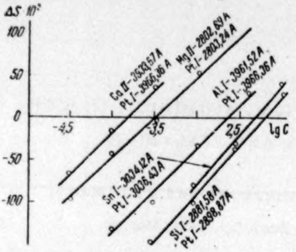

Fig. 1

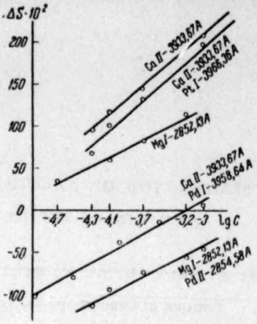

Fig. 2

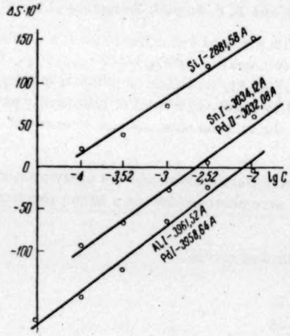

Fig. 3

The calcium content of the original platinum was found by extrapolation to be 0.002%.

Standard solutions for the determination of Ca, Mg, Al, Si, and Sn in refined palladium were prepared in the same way as for platinum. The original palladium contained 0.003% each of calcium and magnesium. After purifying the palladium by means of palladozammine the content of these impurities was lowered to 0.0012% for calcium, and 0.0005% for magnesium. Nevertheless, even after five reprecipitations of palladium as $(NH_3)_2Cl_2Pd$ the calcium and magnesium contents did not decrease.

The palladozammine which had been reprecipitated several times (up to five times) was then reduced in a stream of hydrogen; 6, 2, and 1% solutions were then prepared from the palladium formed, for this purpose the aliquots of palladium were dissolved in aqua regia (both the hydrochloric and nitric acids were redistilled beforehand in quartz vessels).

The nitric acid was then removed by careful boiling with concentrated hydrochloric acid. As the nitrogen oxides were removed the solution was diluted with water and then evaporated to minimum volume, the solution was transferred to a standard flask and made up to the mark with water.

The content of calcium, magnesium, aluminum, and tin in the standard solution prepared was varied from 0.2 to 0.006%, and that of silicon from 0.1 to 0.0003% with respect to the palladium. The palladium concentrations of the solutions were 0.5 and 1%.

The solutions were poured into the sprayer and sprayed in the course of three minutes into the arc between carbon electrodes, the interelectrode distance being 3 mm; fresh solution was passed into the sprayer every minute. The reference line was that of palladium; in addition, the background near the analytical line was also used.

In the case of the 1% solution of palladium which gave very intense lines differing strongly from the analytical line of the test element, platinum was added as an internal standard, the concentration of the platinum being 0.1%.

The background was photographed in those cases where the lines of the internal standard were either far from the analytical line of the test element, or where they possessed incommensurable intensity. Calibration curves obtained by making photometric measurements on the basis of the background, and those obtained on the basis of the lines of platinum or palladium as reference lines, had the same slope to the concentration axis. (Figs. 2 and 3).

The analytical lines used were:

Ca II – 3933.67 – Pd I – 3958.64
Pd I – 3922.96
Mg I – 2852.13 – Pd II – 2854.58
Al I – 3961.52 – Pd I – 3958.64
Sn I – 3034.12 – Pd II – 3032.08
Si I – 2881.58 – – background

The accuracy of determination when the spectra of the same solution was photographed several times on the same plate, or on another plate of the same type was not less than 6-7%.

The sensitivity for determinations in platinum and palladium solutions amounted to: $1 \cdot 10^{-5}$ % Ca, $3 \cdot 10^{-5}$ % Mg, $1 \cdot 10^{-4}$ % Al, $1 \cdot 10^{-4}$ % Si, $3 \cdot 10^{-4}$ % Sn.

The original palladium was found by the extrapolation method to contain 0.001% Ca and 0.0005% Mg.

SUMMARY

A method has been developed for the spectrographic determination of calcium, magnesium, aluminum, silicon, and tin in refined platinum and palladium, in which the metals are brought into solution beforehand. Recommendations are given for the preparation of reference solutions.

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QUANTITATIVE DETERMINATION OF FLUORIDE BASED ON FORMATION OF HYDROXYTRIFLUOROBORATES

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and B. S. Roginskaia

The formation and hydrolysis of fluoroborate complexes has been studied in detail by Ryss and co-workers [1]. They showed that on mixing hydrofluoric and boric acids, there occurs almost immediate formation of hydroxyfluoroboric acid:

$$3HF + H_3BO_3 = HBF_3OH + 2H_2O \qquad (1)$$

Hydroxyfluoroboric acid HBF_3OH is a strong acid which dissociates to give H^+ and BF_3OH^- ions.

At the same time formation of tetrafluoroborates occurs in solution:

$$HF + HBF_3OH = HBF_4 + H_2O. \qquad (2)$$

Reaction (2) is significantly slower than reaction (1) and is catalyzed by H^+ ions.

Formation of BF_3OH^- ions in solution is given as an explanation by I. G. Ryss for the impossibility of carrying out an accurate alkalimetric determination of HBF_4.

Taking into account the high rate of reaction (1) and the low rate of reaction (2), particularly at low hydrogen ion concentrations, we tried to develop a method for the quantitative determination of F^-, based on the alkalimetric titration of the borax formed according to the reaction:

$$3NaF + 5H_3BO_3 = NaBF_3OH + Na_2B_4O_7 + 7H_2O. \qquad (3)$$

Solutions with a known concentration of fluoride were prepared by dissolving accurately weighed aliquots of sodium fluoride in twice-distilled water.

The sodium fluoride was prepared from chemically pure recrystallized sodium carbonate and 40% hydrofluoric acid. The latter was prepared by diluting liquid hydrogen fluoride with twice-distilled water in a platinum basin.

The liquid hydrogen fluoride contained not more than 0.173% H_2SiF_6, 0.013% SO_4^{2-}, 0.141% SO_2, heavy metals 0.004%, and nonvolatile residue 0.0085%.

The sodium fluoride was prepared by adding sodium carbonate to the 40% hydrofluoric acid in such amount that 95% of the acid was neutralized. The solution was evaporated slightly and the precipitated NaF filtered, the NaF was then recrystallized and calcined at 400°.

The crystals showed a neutral reaction to phenolphthalein. In order to control the purity of the product thus obtained, aliquots of the crystals were treated three times in a platinum basin with redistilled, chemically pure hydrochloric acid, after each hydrochloric acid treatment the mass was evaporated to dryness; the product obtained was calcined at about 600° and weighed. The following results were obtained: 0.1672 and 0.7914 g of NaF yielded 0.2341 and 1.1022 g of NaCl; the theoretical amounts of NaCl were 0.2329 and 1.1023 g.

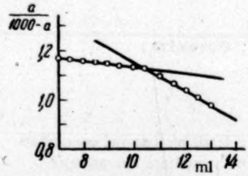
An aliquot of sodium fluoride was dissolved in 30% boric acid solution and the solution obtained titrated conductometrically with hydrochloric acid.

The setup used for conductometric titration consisted of a ZG-4 sonic generator, a drum rheocord, and a resistance box. The null instrument was a four tube a.c. null indicator. Measurements were carried out at a frequency of 1000 cycles.

A glass vessel with fused-in platinized platinum electrodes was used. The vessel constant was $0.8622\ cm^{-1}$. The experimental results are given in Table 1.

From the diagram it is evident that the end point can be determined quite clearly; in all cases, however, the results obtained were 2-5% low (see Table 1).

The low results obtained can be explained by the hydrolysis of $NaBF_3OH$ with formation of borofluoride complexes with a lower fluorine content. In order to prevent hydrolysis, in subsequent analyses the solution was diluted with an equal volume of ethanol. Results of these determinations are given in Table 2.



Conductometric titration curve.

As the results given in Table 2 show, titration of solutions containing up to 0.1 g of fluoride can be carried out with an accuracy of ± 0.3 %. For lower fluoride contents the error increases slightly, and, at fluoride contents of 0.02 – 0.04 g of fluoride, it amounts to ± 0.8 %.

TABLE 1

Determination of Fluoride as $NaBF_3OH$ in Aqueous Solutions

F taken, in g	F found, in g	Relative error, in %
0,0190	0,0186	−2,1
0,0190	0,0182	−4,2
0,0190	0,0183	−3,7
0,0474	0,0464	−2,1
0,0950	0,0924	−2,7
0,1900	0,1820	−4,2
0,0950	0,0904	−4,8

TABLE 2

Determination of Fluoride in Aqueous-Alcoholic Solution as $NaBF_3OH$

F taken, in g	F found, in g	Relative error, in %
0,2488	0,2483	−0,20
0,1967	0,1970	+0,15
0,1893	0,1892	−0,05
0,1727	0,1732	+0,29
0,1516	0,1518	+0,13
0,0917	0,0916	−0,11
0,0650	0,0653	+0,46
0,0394	0,0391	−0,76
0,0206	0,0207	+0,48
0,0463	0,0465	−0,43

Taking into account the possibility that reaction (2) occurs, in some cases, conductometric titrations were carried out 24 hours after mixing. The analytical results obtained under these conditions were the same as those obtained previously. The effect of various anions on the accuracy of fluorine determination was also studied.

As the results given in Table 3 show, strong acid anions (SO_4^{2-}, NO_3^-, Cl^-) present as impurities, increase the relative experimental error to 1%.

In the presence of considerably larger amounts of these impurities the relative error increases to 4 %.

Weak acid anions interfere with the determination. Presumably, all cations which give precipitates at a pH of 7.5 should interfere with fluorine determination by this method.

In view of the interest in determining the fluoride content of heavy metal fluorides, the technique described was used for determining fluoride in cobalt, manganese, and antimony fluorides.

TABLE 3

Effect of Various Anions on the Accuracy of Fluoride Determination

Impurity	Ratio of NaF: impurity (g/mole)	Weight of F taken, in g	F found, in g	Relative error, in%
NaCl	1:9	0.1423	0.1366	−4
NaCl	1:1.5	0.1900	0.1903	+0.16
NaCl	1:1	0.2014	0.2025	+0.54
Na_2SO_4	3:1	0.0385	0.0383	−0.52
Na_2SO_4	1:10	0.1908	–	–•
$NaNO_3$ + +NaCl + +Na_2SO_4	1:1	0.2185	0.2165	−0.92••
$NaNO_3$ + +NaCl + +Na_2SO_4	1:1	0.1818	0.1835	−0.93••

•A precipitate formed on addition of alcohol.

••Equal amounts (in g-mole) of NaCl, Na_2SO_4, and $NaNO_3$ taken.

TABLE 4

Determination of Fluoride in Co, Mn, and Sb Salts

Test mixture	Fluoride taken, in g	Fluoride found in g	Relative error, in %
$Co(NO_3)_2$	0.1393	0.1400	+0.50
$Co(NO_3)_2$	0.1371	0.1384	+0.95
$Co(NO_3)_2$	0.1477	0.1485	+0.55
$MnCl_2$	0.1362	0.1350	−0.88
$MnCl_2$	0.1384	0.1386	+0.14
$SbCl_3$	0.1363	0.1358	−0.37
$SbCl_3$	0.1394	0.1409	+1.08
$SbCl_5$	0.1814	0.1803	−0.61
$SbCl_5$	0.1519	0.1534	+0.98

In view of the difficulty of preparing the fluorides of the metals indicated, with a known fluoride content, we determined fluoride in mixtures of sodium fluoride with the equivalent amounts of $Co(NO_3)_2$, $MnCl_2$, $SbCl_3$, and $SbCl_5$.

Analytical procedure. An accurately weighed aliquot of sodium fluoride was mixed with an aliquot of one of the salts indicated. The mixture was treated with an appropriate amount of 1 N NaOH, taken in an excess of 1.5 and 2 with respect to the mixture, and the whole boiled for one hour. The alkali treatment was carried out in 250 ml stoppered conical flask. The stopper was fitted with two tubes for passage of oxygen purified from CO_2, and with a dropping funnel for adding water, when necessary, to the flask. The precipitate was filtered through a fine filter and then washed with hot water until the total volume of filtrate obtained was 250 ml (the filtrate and wash liquors were collected in a 250 ml standard flask); 50 ml of this solution was transferred to the titration flask, where it was neutralized with 0.1 N hydrochloric acid using phenolphthalein as indicator; 1.2 g of boric acid was added, followed by 50-60 ml of distilled ethanol, and, after cooling to room temperature, the solution was titrated conductometrically with 0.1 N HCl.

As the results given in Table 4 show, the relative experimental error for determination of fluoride does not exceed 1.1%. When the test material does not contain Co, Mn, Sb etc., the alkali treatment is not given.

SUMMARY

A method has been developed for the quantitative determination of fluoride which is based on conductometric titration of the borax formed during the reaction: $3NaF + 5H_3BO_3 = NaBF_3OH + Na_2B_4O_7 + 7H_2O$.

The method has been applied to the determination of fluoride in cobalt, manganese, and antimony fluorides.

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*Original Russian pagination. See C. B. Translation.

NEW COLOR REACTIONS FOR FERRICYANIDES

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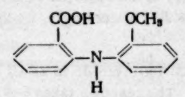
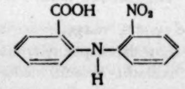
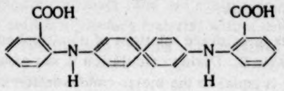
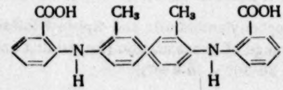
Despite the fact that in recent years a fairly large number of color reactions have been suggested for the ferricyanide ion, very few photometric methods are known for its determination. This is a consequence of the fact that the final reaction product is, in most cases, a precipitate which may have different colors. Almost all the known reactions for ferricyanides are based on the capacity of the latter to oxidize certain organic materials (benzidene, p-phenetidine, o-toluidine, and α-naphthylamine [1], dimethyl- and diethylanilines [2], dimethylaminoantipyrine and tetramethyldiaminodiphenylmethane [3]) to form brightly colored reaction products. The sensitivity of such reactions can be increased considerably by removing the ferricyanide ions from the reaction sphere by precipitation with zinc ions. Further, reagents which are organic bases are often precipitated by ferricyanides. In the absence of zinc ions the reaction has a low sensitivity.

All the reactions mentioned are not very specific, since similar reactions are given in an acid medium by most strong oxidizing agents.

TABLE 1

Sensitivity of Certain Diphenylaminecarboxylic Acids Toward the Ferricyanide Ion

Acid	Formula	Color of the reaction product	Sensitivity, γ/ml
o'-Methoxyphenylanthranilic acid		Red	23,0
o'-Nitrophenylanthranilic acid		Brown-yellow	1,0
Diphenylbenzidene-o,o'-dicarboxylic acid		Red-brown	2,3
Diphenyltolidine-o,o'-dicarboxylic acid		Brown-red	0,5

Willard and Monalo [4] have shown that certain substituted diphenylaminecarboxylic acids are capable of being oxidized by ferricyanides in alkaline media to form colored products. These reactions are highly specific

TABLE 2

Molar Extinction Coefficients of the Reagents Studied

V_{total}, in ml	$V_{reagent}$, in ml	$C_{original}$, in moles	Molar conc. of the oxidation product	ϵ	ϵ_{molar}
For diphenyltolidine-o,o'-dicarboxylic acid					
5	0,34	10^{-3}	$0,68 \cdot 10^{-4}$	1,23	$3,63 \cdot 10^{4}$
10	0,34	10^{-3}	$0,34 \cdot 10^{-4}$	0,66	$3,59 \cdot 10^{4}$
10	0,68	10^{-3}	$0,68 \cdot 10^{-4}$	1,23	$3,63 \cdot 10^{4}$
				Average	$3,62 \cdot 10^{4}$
For o'-nitrophenylanthranilic acid					
4	0,33	10^{-3}	$0,63 \cdot 10^{-4}$	0,21	$0,67 \cdot 10^{4}$
4	1,00	10^{-3}	$2,5 \cdot 10^{-4}$	0,62	$0,64 \cdot 10^{4}$
				Average	$0,65 \cdot 10^{4}$

TABLE 3

Determination of Potassium Ferricyanide in Potassium Ferrocyanide by Means of Diphenyltolidene-o,o'-dicarboxylic Acid

Taken, in γ	Found, in γ	Taken, in γ	Found, in γ
30	28	3.0	3.2
65	66	12.0	11.4
90	90	8.5	8.5

for ferricyanides (in alkaline media almost all known strong oxidizing agents do not oxidize diphenylamine derivatives).

We have studied the sensitivity of the detection of ferricyanide ions in a medium of 5 N NaOH by a spot technique using the following diphenylaminecarboxylic acids: phenylanthranilic, and meta-N-phenylaminobenzoic acids, o,o'-diphenylaminedicarboxylic acid and its meta- and para isomers, the three isomeric tolylanthranilic acids, o-methoxyphenylanthranilic, o'- and para'-nitrophenylanthranilic acids, and diphenylbenzidene-o,o'-dicarboxylic acid. The most sensitive reagents are given in Table 1. The sensitivity of the diphenylaminecarboxylic acids toward ferricyanide ions drops rapidly with increasing alkali concentration (starting at 1 N and higher). The sensitivity of the reaction with o-nitrophenylanthranilic acid starts to drop even in a medium of 0.3 N sodium hydroxide. Accordingly, for this acid, the sensitivity was determined in a medium of 0.1 N sodium hydroxide.

The reagents studied form, with potassium ferricyanide in alkali solution, red-brown solutions with a maximum light absorption at 470 mμ (Fig. 1). The reaction takes 3-4 minutes to go to completion.

The results obtained during a study of the system "reagent—ferricyanide ion" by the Ostromyslenskii-Job-Babko method are shown in Figs. 2 and 3; they show that diphenylamine derivatives in alkali media are oxidized according to a scheme similar to that for their oxidation in acid media; two equivalents of the oxidizing agents are used up for oxidizing the organic molecule.

The molar extinction coefficients of oxidized solutions of o'-nitrophenylanthranilic and diphenyltolidine-o,o'-dicarboxylic acids are given in Table 2. During calculation it was assumed that the molar concentration of the colored reaction product formed is equal to the molar concentration of the acid taken for oxidation.

The oxidation products of o-nitrophenylanthranilic and diphenyl tolidenedicarboxylic acids conform to the Lambert—Beer law over a certain range of concentration (for the first acid over the range 10-100 γ in 5 ml, and for the second acid over the range 30-300 γ in 4 ml).

Preponderant amounts of ferricyanides do not interfere with the reaction.

Photometric determination of traces of ferricyanide in potassium ferrocyanide is carried out as follows: to 0.1-1.0 ml of test solution containing not more than 100 γ / ml of ferricyanide ion, and contained in a test

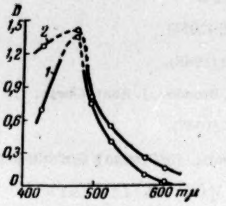


Fig. 1. Light absorption curves of the oxidized products of o-nitrophenylanthranilic acid (I) and diphenylbenzidene-o,o'-dicarboxylic acid (II).

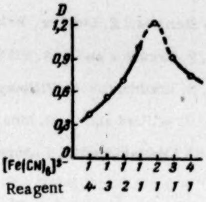


Fig. 2. The system ferricyanide—diphenyltolidene-o,o'-dicarboxylic acid (V_{total} – 5 ml; $C_{original}$ – 10^{-3} M; λ – 480 mμ; d – 5 mm; 0.05 N KOH.

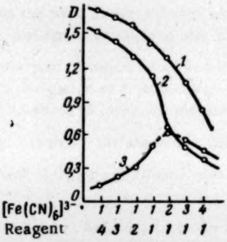


Fig. 3. The system ferricyanide—o-nitrophenylanthranilic acid: V_{total} – 4 ml; V – 3 ml; $C_{original}$ – 10^{-3} M; λ – 480 mμ; d – 5 mm; 0.05 N KOH; I) reagent–reaction product; II) reagent; III) reaction product.

tube is added 0.2 ml of a 0.1% solution of the reagent (o-nitrophenylanthranilic or diphenyltolidene-o,o'-dicarboxylic acid) in a 0.1% solution of sodium carbonate. After mixing, the contents of the test tube are made up to a volume of 5 ml with 0.05 N sodium or potassium hydroxide. The solutions are left for 5 minutes after which photometric measurements are made at 470 mμ in a cell with a layer thickness of 5 mm. Water is used as the compensating liquid. A calibration curve can be constructed by means of a solution of recrystallized potassium ferricyanide [5]. Some idea of the accuracy of the method is given in Table 3.

Synthesis of reagents. o-Nitrophenylanthranilic acid was synthesized according to Ullmann's method [6]. Diphenyltolidene-o,o'-dicarboxylic acid* was synthesized in similar fashion to diphenylbenzidene-o,o'-dicarboxylic acid [7]. The synthesis was carried out as follows: a mixture of 3 g of o-chlorobenzoic acid, 2 g of o-tolidene, 2.7 g of potassium carbonate, and 20 ml of isoamyl alcohol was heated to the boil for 2 hours in the presence of a small amount of "naturkupfer C." Excess isoamyl alcohol was removed by steam distillation, after which the reaction product was precipitated by means of 1 : 1 hydrochloric acid. The acid obtained was filtered on a Buchner funnel and dried at 110°. 2.75 g of crude was obtained, this was purified by dissolving it in a 0.1% solution of sodium carbonate, and was again precipitated with dilute hydrochloric acid. Diphenyltolidene-o,o'-dicarboxylic acid is a powdery material with a dark-green color, and has a rather ill-defined melting point at about 300°. The following results were obtained during a nitrogen determination:

Calculated for $C_{23}H_{24}O_4N_2$, nitrogen 6.19%.

Found for $C_{23}H_{24}O_4N_2$, nitrogen 6.03%.

SUMMARY

The new color reactions are described for the ferricyanide ion; photometric methods of determining potassium ferricyanide in the presence of large amounts of potassium ferrocyanide have been developed on the basis of these reactions.

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*We are the first to prepare this reagent.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF WATER OF CRYSTALLIZATION IN CERTAIN CRYSTALLOHYDRATES ON THE BASIS OF THEIR ABSORPTION SPECTRA IN THE NEAR INFRARED (0.8 – 2.5 μ)

D. S. Gorbenko-Germanov, R. A. Zenkova and T. L. Bolotina

The present article contains a description of a method for the quantitative determination of water of crystallization on the basis of the infrared absorption spectra in the 0.8 – 2.5 μ region of crystallohydrates in the solid phase. Milligram amounts of test material are necessary in order to get reliable results by this method.

The spectrum of liquid water in the region 0.8 – 2.5 μ [1-2]. In order to choose an analytical band for subsequent investigation of crystallohydrates, absorption spectra were taken in the 0.8 – 2.5 μ region for a layer thickness of 0.046 – 100 mm. All measurements were carried out on a IKS-11 infra-red spectrometer.

In Fig. 1 is shown the absorption spectrum of water in the 0.8 – 2.5 μ region.

The band H_2O_{liquid} 5130 cm^{-1} was chosen as the analytical band on the basis of the following considerations:

1. The band at 5130 cm^{-1} has the greatest intensity.

2. At wavelengths shorter than 1.9 μ there was observed a continuous absorption, determined by the low transparency of the solid preparations in the wavelength shorter than 1.9 μ.

The technique used for taking spectra of preparations in the solid phase. Some modifications were made to the standard IKS-11 model, since the apparatus as it stood did not ensure the necessary accuracy of measurement.

a) The recorder used was one taken from a MF-4 microphotometer which had a more accurate recording scale (1000 mm long with 1 mm divisions) and permitted the spectra to be photographed on a plate.

b) More accurate apparatus was used for controlling the heating current in the FEOU-15 amplifier (a millivoltmeter with a scale of 17 millivolts and an universal M-16 measuring apparatus were used).

c) For more accurate deciphering of the spectra, the datum lamp was provided with an additional button, by means of which it was possible to direct vertical datum lines onto the spectrograms for an arbitrary reading of the wavelength drum.

d) So that it should be possible to photograph the spectra of dense samples, the FEOU-15 amplifier was operated in its high range (tube 2.5 volts, 0.55 amp. at a voltage of 2.4 volt).

In order to take photographs of the absorption spectra of samples in a solid state, the technique of pressing in an optically inactive diluent was used (calcined, ground potassium chloride, which is transparent up to 20 μ). The mixtures, containing varying amounts of the crystallohydrate were pressed into tablets in a hydraulic press. At a pressure of 220-230 kilos / cm^2, and for a diameter of the press-form of 12 mm, and 117 mg of test mixture, tablets with a thickness of 0.55 ± 0.01 mm were obtained. The tablet thickness was measured to an accuracy of 0.01 mm with a micrometer.

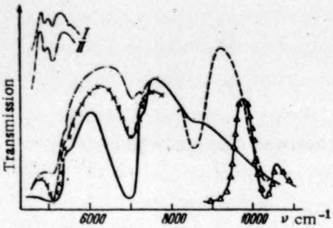

Fig. 1. Absorption spectra of H_2O_{liquid} in the 5000-11000 cm^{-1} region.
I and II) absorption spectra of $Eu_2(SO_4)_3 \cdot 8H_2O$ —·—·— 0.74% water, tablet thickness 1.23 mm; – – – – – *0.4% water, tablet thickness 1.49 mm. Cell thickness: – – – 1 mm; —·—·— 0.046 mm; -x-x-x 0.200 mm; – – – – *10 mm; -Δ-Δ-Δ- 100 mm.

When photographs were taken of the absorption spectra of various crystallohydrates it was found that the band at 5130 cm^{-1} in the crystallohydrates, in a number of cases, suffers a shift of 100-200 cm^{-1}.

In Fig. 1 (Curves 1 and 2) and in Fig. 2 is shown the absorption band at 5130 cm^{-1} for various crystallohydrates.

The construction of a calibration curve, and the method of calculating optical density at extreme points. The standard chosen for constructing the calibration curve was the octahydrate of europium sulfate $Eu_2(SO_4)_3 \cdot 8H_2O$; the latter was chosen for the following reasons:

1) This crystallohydrate is highly stable;

2) It is possible to control the stability of this compound during the process of taking the infrared absorption spectra, on the basis of the nature of the splitting of the electronic bands of Eu^{3+} which is observed in the 4000-5500 A region (a sharp quintet in the 4600 A region and a sharp triplet in the 5200 A region [3]). Control was realized by means of a ISP-51 spectrograph with a camera with F = 800 mm.

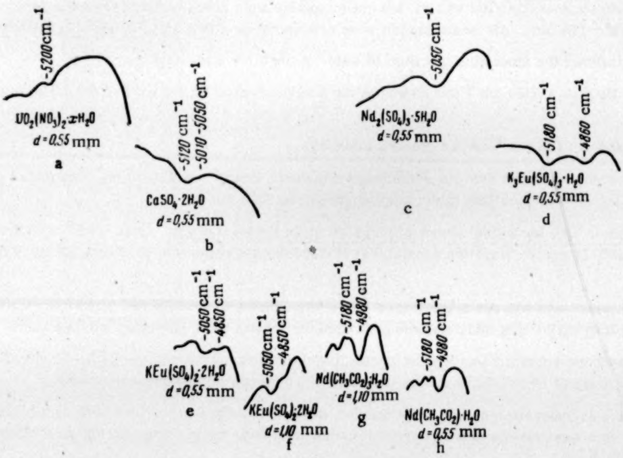

Fig. 2. The band H_2O_{liquid} 5130 cm^{-1} in certain crystallohydrates:
a) $UO_2(NO_3)_2 \cdot H_2O$ (d = 0.55 mm); b) $CaSO_4 \cdot 2H_2O$ (d = 0.55 mm); c) $Nd_2(SO_4)_3 \cdot 5H_2O$ (d = 0.55 mm); d) $K_3Eu(SO_4)_3 \cdot H_2O$ (d = 0.55 mm); e) $KEu(SO_4)_2 \cdot 2H_2O$ (d = 0.55 mm); f) $KEu(SO_4)_2 \cdot 2H_2O$ (d = 1.10 mm); g) $Nd(CH_3COO)_3 \cdot H_2O$ (d = 1.10 mm); h) $Nd(CH_3COO)_3 \cdot H_2O$ (d = 0.55 mm).

In order to construct a calibration curve within the coordinates optical density and water content, amounts of europium sulfate octahydrate varying from 0.5 to 21.1 mg were used for making tablets with a weight of 117 mg (0.078 – 3.52% of water or 0.09 – 4.12 mg of water in a tablet).

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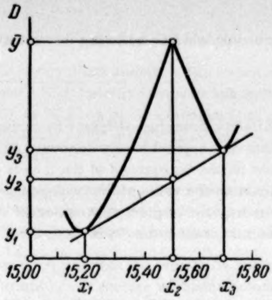
*As in original – Publisher.



Relative divisions of the wavelength drum of the monochromator

Fig. 3. Calculation of the optical density at the extreme points.

In order to determine the position of the three extreme points corresponding to the maximum transmission of the tablets on both sides of the absorption maximum (x_1 and x_3), and the point of maximum absorption (x_2) (Fig. 3), a qualitative photograph of the spectra was taken using additional datum lines. Subsequently, measurements were only made at these three points; when a switch was made to another crystallohydrate for which a shift in the absorption band was observed, a qualitative photograph was again taken and the extremal points x_1, x_2, and x_3 determined and measurements then carried out only at these three points.

For calculating the value of $\overline{y} - y_2$ it is possible to use the general form of the equation for a straight line

$$y = Ax + B \qquad (1)$$

For the points x_1, x_2, and x_3 it is possible to write three equations:

$$y_1 = Ax_1 + B; \qquad (2)$$
$$y_2 = Ax_2 + B; \qquad (3)$$
$$y_3 = Ax_3 + B. \qquad (4)$$

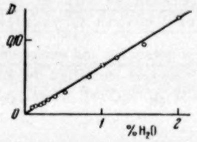


Fig. 4. Calibration curve.

By removing A and B from (2) and (4) and substituting their values in (3) we get:

$$y_2 = \frac{x_2(y_1 - y_3) + x_1y_3 - x_3y_1}{x_1 - x_3} \qquad (5)$$

In the case of $Eu_2(SO_4)_3 \cdot H_2O$, the points x_1, x_2, and x_3 had the values 15.20, 15.52, and 15.70 respectively (relative divisions of the wavelength drum).

Substituting these values in (5) and simplifying, we get:

$$y_2 = 0.36y_1 + 0.64\ y_3 \qquad (6)$$

or the value of D at the absorption maximum is given by

$$D = \overline{y} - y_2 = \overline{y} - 0.64\ d_1 - 0.36\ d_2, \qquad (7)$$

where d_1 and d_2 are the optical densities at points x_3 and x_1 respectively, while $\underline{y}$ is the optical density at the maximum absorption band.

In the case of another crystallohydrate, new values of x_1, x_2, and x_3 are substituted in (5) and a new equation derived.

Determinations were carried out by measuring the transmission of tablets containing the crystallohydrates at the extreme points, and then the transmission of potassium chloride tablets was measured immediately at the same points.

The optical density was calculated by the well-known equation

$$D = \log \frac{I_0}{I} = K_\nu cd, \qquad (8)$$

where I_0 and I are the transmissions of tablets of potassium chloride and of tablets containing the crystallohydrates respectively.

Results obtained by this method are presented graphically in Fig. 4.

It was observed that potassium chloride tablets measured at different times had different transmissions at the extreme points, while the ratio of the transmissions at these points kept approximately constant. This fact permitted the determination of the mean ratios of the transmissions for the background of the tablets at the extreme points (point x_1 being taken as unity), and helped us to calculated the value of the background at points x_2 and x_3 (the transmission of the test sample, and the value of the background at point x_1, were equal to one another). Under these conditions the third member on the right hand side of equation (7) became zero.

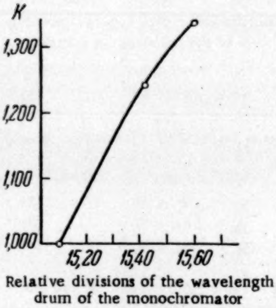


Fig. 5. Relation between the mean values of the background and the relative divisions of the wavelength drum of the monochromator.

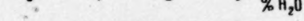


Fig. 6. The calibration curve for the method of the mean values of the background at the extreme points.

Using this method all former test samples prepared at various times and photographed for various slit widths of the monochromator were recalculated. The calibration curve obtained is shown in Fig. 6.

The simplicity of the calculation, the short time taken to make measurements, and also the small relative error in the determination of the optical density enabled us to determined the amount of water of crystallization in various crystallohydrates.

The Quantitative Determination of the Water of Crystallization of Certain Crystallohydrates

1) Double sulfates of potassium and europium. For the system $K_2SO_4 - Eu_2(SO_4)_3 - H_2O$ we identified the following individual compounds: $KEu(SO_4)_2 \cdot H_2O$ (1), $KEu(SO_4)_2 \cdot 2H_2O$ (2), $K_3Eu(SO_4)_3 \cdot H_2O$ (3).

For compounds (1) and (2) the position of the extreme points coincided with that found for europium sulfate octahydrate, and the calculation was made according to the equation $D = \bar{y} - 0.64\, d_1$.

In the case of compound (3), the points x_1, x_2, and x_3 had the following values: 15.20, 15.64, and 15.75 and calculations were made according to the equation: $D = y - 0.80\, d_1$.

Fifteen samples (from 7.22 to 23.13 mg of compound in a tablet) were taken for analysis of (1); the mean value amounted to 4.6% of water (theoretical water content – 4.49%; 5.3% by gravimetric analysis).

For the analysis of (2), 12 samples were taken (from 8.58 to 17.64 mg of compound in a tablet); mean value 7.4% water (theoretical water content 8.59%; 8.7% by gravimetric analysis).

Four samples (from 24.97 to 38.50 mg in a tablet) were taken for the analysis of (3); mean value, 2.8% of water (theoretical water content 3.13%; by gravimetric analysis 3.0%).

The results obtained confirm the composition of compounds (1), (2), and (3).

2. Neodymium sulfate. Calculations were made on the basis of $D = \bar{y} - 0.64\, d_1$; the position of the extreme points coincided with that found for europium sulfate octahydrate $Eu_2(SO_4)_3 \cdot 8H_2O$. Nine samples, 6.28 mg per tablet were taken for analysis; the mean value found was 12.4% (theoretical water content calculated on the basis of the formula $Nd_2(SO_4)_3 \cdot 5H_2O$ 13.51%); by gravimetric analysis 10.0%.

These results confirm the composition $Nd_2(SO_4)_3 \cdot 5H_2O$.

3. Neodymium acetate. The experimental points x_1, x_2, and x_3 for this compound had the values 15.22, 15.48, and 15.62; calculations were made on the basis of the equation $D = \overline{y} - 0.65\ d_1$. Six samples containing from 12.8 to 28.5 mg of the compound per tablet were taken; the average value found for the water was 5.2% (the theoretical water content based on the formula $Nd(CH_3COO)_3 \cdot H_2O$ is 5.3%). The compound was not analyzed gravimetrically.

4. Calcium sulfate. The experimental points x_1, x_2, and x_3 for this compound were 15.42, 15.58, and 15.75; calculations were made on the basis of the euqation $D = \overline{y} - 0.33\ d_1$. Three samples each containing 6.56 g of the compound per tablet, were taken for analysis; the mean value found for water was 19.0% (the theoretical water content based on a formula of $CaSO_4 \cdot 2H_2O$ is 20.9%; the value found gravimetrically was 20.6%). The results obtained confirm the formula $CaSO_4 \cdot 2H_2O$.

This method permits determination of micro amounts of water in samples, the weight of which would not allow reliable gravimetric determination. The amount of test material in which it would still be possible to determine the water content reliably, can be decreased a few times more by using tablets with a smaller diameter and thickness.

SUMMARY

1. The absorption spectrum of H_2O_{liquid} in the 0.8-2.5μ region has been studied. The H_2O_{liquid} band at 5130 cm^{-1} is displaced by 100-200 cm^{-1} in crystallohydrates, and, in some cases, splits up. The shift and the splitting of the band at 5130 cm^{-1} testifies to a fairly deep penetration of the water molecules into the crystallohydrate molecule.

2. Calibration curves have been obtained and methods of calculating optical density at three extreme points are suggested. A method is described for the determination of water of crystallization in crystallohydrates.

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NEW METHODS FOR THE QUANTITATIVE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS

II. GRAVIMETRIC DETERMINATION OF CHLORINE, BROMINE, AND IODINE

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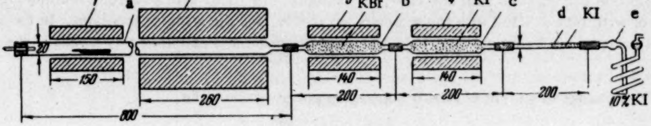
All published methods for the quantitative determination of chlorine, bromine, and iodine can be divided into two main groups – gravimetric and volumetric. All the gravimetric methods are based on combining the halogen with silver and then weighing the silver halides.

In our first communication [1] we described new quantitative volumetric methods of determining chlorine, bromine, and iodine in organic materials. In the present article a description is given of new gravimetric methods for the quantitative determination of each of the elements indicated, which do not involve the use of silver.

The new gravimetric methods of determining the halogens are based on differences in their chemical activity. The organic compound is broken down by one of the published methods, for example, by combustion in an atmosphere of oxygen or in air. The gaseous reaction products, containing the free halogens, and the hydrogen halides, are passed through two heated tubes filled in succession with metal bromides (see diagram). In the first tube b bromine ions are oxidized by the free chlorine, while in the second tube c iodine ions are oxidized by the liberated bromine. In the third tube d, filled with moist potassium iodide, the liberated iodine is trapped quantitatively. A Winkler apparatus is connected to tube d, this apparatus being filled with a solution of 10% potassium iodide for trapping traces of iodine carried through by the oxygen stream. The chlorine and bromine contents of the test sample are then calculated on the basis of the changes in weight of tubes b and c. The iodine content of the test sample is calculated from the difference between the total amount of iodine condensed in tube d and trapped by the Winkler apparatus, and the amount of chlorine and bromine found from the changes in weight of tubes b and c. In this way it is possible to determine chlorine, bromine, and iodine separately on one aliquot of test material. Methods for the quantitative determination of two and three halogens on one aliquot of test material will be described in a future article.



EXPERIMENTAL

a) Quantitative determination of chlorine. The apparatus is assembled (see diagram). Tube d is moistened with water; it is then dipped in a bottle of potassium iodide and 2-3 g of this compound introduced into it, care being taken to ensure that the potassium iodide is not too closely packed so as to hold up the passage of the gases

TABLE 1

Gravimetric Determination of Halogens

Test material	Weight of sample in g	Decrease in tube wt. g	% Halogen			Tube filled with:
			calc.	found	difference	
Hexachloroethane	0,1104	0,1244	89,89	89,86	−0,03	KBr
"	0,0742	0,0836	89,89	89,85	−0,04	KBr
"	0,0956	0,1078	89,89	89,92	+0,03	NaBr
"	0,1174	0,1322	89,89	89,80	−0,09	NaBr
"	0,1338	0,3102	89,89	89,87	−0,02	KI
Polyvinylchloride	0,0921	0,1350	56,73	56,82	+0,09	KI
Dibromobenzene	0,0722	0,0288	67,76	67,81	+0,05	KI
"	0,0562	0,0224	67,76	67,74	−0,02	KI

through it. 5-8 ml of a 10% solution of potassium iodide is poured into the Winkler apparatus. The first oven is heated to 750-800°, while the second is heated to 800-900°, an the third and fourth heated to 650-680° and 450-500° respectively. The temperature of the third and fourth ovens is measured by means of thermocouples.

Purified and dried oxygen is passed at the rate of 150-200 ml/minute for 15-20 minutes through the apparatus with the ovens switched on. The absorption apparatus is then disconnected. The tubes filled with bromide and iodide are sealed with rubber caps and transferred to the balance room, where they are allowed to cool (30-40 minutes), they are next weighed and reconnected to the apparatus. Test material is weighed out into a boat, and powdered quartz sand or chromium oxide strewn over it. When chromium oxide is used [2] combustion proceeds better, but this oxide cannot be used repeatedly because of loss in activity. The boat and sample are placed in the combustion tube at a distance of 2-3 cm from the point at which the tube enters the first oven. By gradually shifting the oven [1] the sample is set alight or is evaporated. The vapors from the material and its decomposition products pass with the oxygen stream into the calcining zone, where its complete breakdown occurs. This process takes 10 to 30 minutes depending on the nature of the test material. Finally the tube is heated strongly along the whole of its length for another 5-10 minutes. The absorption apparatus is disconnected again and tubes b and c covered with the rubber caps; they are removed to the balance room, and after 30-40 minutes weighed (without the rubber caps). The contents of tube d and of the Winkler apparatus are transferred quantitatively by washing into a flask in which the solution is titrated with 0.05 N sodium thiosulfate. For evaporating the material and heating the tubes filled with potassium bromide and iodide, it is expedient to use hinged ovens.

Calculation of the chlorine content (in %) can be carried out as follows:

1. From the change in weight of tube b containing potassium (sodium) bromide.
2. From the change in weight of tube c containing potassium iodide.
3. From the weight of iodine condensed in tube d and the Winkler apparatus.

If desirable one can manage with one tube, for example, one filled with potassium bromide b, or potassium iodide c, or with tube d filled with moist potassium iodide, and the Winkler apparatus. In the last instance, determination is carried out volumetrically [1]. The chlorine content is calculated by means of the following formulas:

1. From the change in weight of tube b containing potassium bromide

$$\%\mathrm{Cl} = \frac{\mathrm{Cl} \cdot b_1 \cdot 100}{a\,(\mathrm{Br} - \mathrm{Cl})} ;$$

where Cl is the gram-equivalent of chlorine; b_1 is the decrease in weight of the tube containing potassium bromide; a is the weight of test material.

2. From the change in weight of tube c containing potassium iodide

$$\% \mathrm{Cl} = \frac{\mathrm{Cl} \cdot b_2 \cdot 100}{a\,(\mathrm{I} - \mathrm{Cl})};$$

where Cl is the gram-equivalent of chlorine; b_2 is the decrease in weight of tube c containing potassium iodide; a is the weight of test material; I − Cl is the difference between the atomic weights of iodine and chlorine.

3. From the amount of iodine liberated

$$\% \mathrm{Cl} = \frac{\mathrm{Cl} \cdot k \cdot 100}{20000 \cdot a},$$

where Cl is the gram-equivalent of chlorine; k is the volume of 0.05 N sodium thiosulfate used in ml; a is the weight of test material.

b) Quantitative determination of bromine. The analysis is carried out in the apparatus shown in the diagram, the tube containing potassium bromide is omitted, however.

The bromine content (in %) is calculated: 1. From the change in weight of the tube c containing potassium iodide:

$$\% \mathrm{Br} = \frac{\mathrm{Br} \cdot b_2 \cdot 100}{(\mathrm{I} - \mathrm{Br}) \cdot a};$$

where Br is the gram-equivalent of bromine; b_2 is the decrease in weight of tube c containing potassium iodide; a is the weight of test material.

2. From the amount of iodine collected in tube d and the Winkler apparatus, and subsequently titrated with sodium thiosulfate

$$\% \mathrm{Br} = \frac{\mathrm{Br} \cdot k \cdot 100}{20000 \cdot a};$$

where Br is the gram-equivalent of bromine, k is the volume of 0.05 N sodium thiosulfate used, in ml; for titrating the liberated iodine; a is the weight of test material.

c) Quantitative determination of iodine. Determination of iodine is carried out in the same way as that indicated for chlorine and bromine, in this case, however, the tube c containing iodide, and tube b with bromide are not included in the apparatus. The contents of tube d and the Winkler apparatus are quantitatively washed into a flask and the iodine titrated with 0.05 N sodium thiosulfate.

The iodine content is calculated by means of the formula:

$$\% \mathrm{I} = \frac{\mathrm{I} \cdot k \cdot 100}{20000 \cdot a},$$

where I is the gram-equivalent of iodine; k is the volume of 0.05 N sodium thiosulfate; a is the weight of test material.

TABLE 2

Gravimetric and Volumetric Determination of Halogens

Test material	Wt. of sample, in g	Change in sample wt. containing:		0.05 N $Na_2S_2O_3$ used for titration, ml	%Halogen from calculations based on KBr			%Halogen from calculations based on KI			%Halogen from calculations based on I		
		KBr, in g	KI, in g		calc.	found	difference	calc.	found	difference	calc.	found	difference
Hexachloroethane	0.0727	0,0820	0,0866	36,84	89,89	89,95	+0,06	89,89	89,85	−0,04	89,89	89,83	−0,06
Dichlorobenzene	0.0388	0,0234	0,0249	10,56	48,23	48,09	+0,14	48,23	48,40	+0,17	48,23	48,25	+0,02
Bromocamphor	0,0 16	—	0,0145	6,20	—	—	—	34,57	34,43	−0,14	34,57	34,60	+0,03
Dibromobenzene	0,0614	—	0,0245	10,40	—	—	—	67,76	67,84	+0,09	67,76	67,68	−0,08

Tables 1 and 2 contain some results illustrating the applicability of the method.

SUMMARY

A new gravimetric (and volumetric) method has been developed for determining chlorine, bromine, and iodine in organic materials, one element at a time; the method is based on differences in the activity of the halogens. The method is simple, and does not require complicated apparatus, expensive reagents, or silver – which is normally employed – or complicated techniques.

Experimental error does not exceed ± 0.1 – 0.2%. An analysis takes 40-50 min. The accuracy of the value obtained for chlorine can be checked in three ways during the determination, while the value for bromine can be checked in two ways. Sulfur interferes with determination of the halogens.

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*Original Russian pagination. See C. B. Translation.

DETERMINATION OF CYCLOHEXANONE AND CYCLOHEXANOL IN EACH OTHERS PRESENCE

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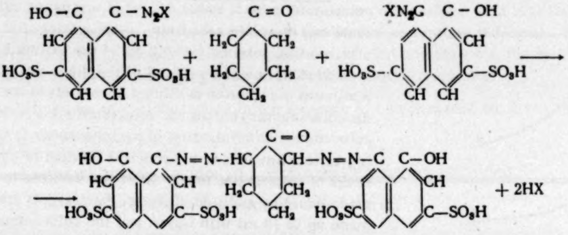
Cyclohexanone and cyclohexanol find wide application as solvents for many organic materials, and as intermediate products in industrial organic synthesis. Methods of determining cyclohexanone and cyclohexanol based on the reactions of their functional groups [1, 2] are complicated to carry out and take a long time; they are normally carried out in a nonaqueous medium and are only applicable to high concentrations. Other methods are based on condensation and polymerization reactions [3, 4, 5] and are only applicable for the determination of each taken separately, or for one in the presence of insignificant amounts of the other.

We have developed a convenient method for the determination of cyclohexanone and cyclohexanol in each others presence. Determination of cyclohexanone is based on its reaction with the diazonium salt of H-acid (1-naphthylamine-8-hydroxy- 3,6-disulfonic acid). We were the first to establish the capacity of cyclohexanone to couple with the diazonium salt of H-acid to form a cherry-red dye according to the equation:



The reaction sensitivity is 0.2 γ/ml. We prepared the azo dye in a pure state and established its composition. The color of solutions obtained during the reaction of cyclohexanone with the diazonium salt of H-acid conforms to the Beer law (Fig. 1). Maximum light absorption is observed at 550 mμ (Fig. 2).

The molar extinction coefficient is 15700.

The diazonium salt of H-acid possesses a sharply expressed capacity to undergo a self coupling reaction in which intensely colored products with a blue color are formed. This fact complicates the use of H-acid in photometric analysis as the diazo component. The addition of sodium sulfite or bisulfite to the test solution, however, prevents this self coupling of diazotized H-acid.

During determination of cyclohexanone in the presence of cyclohexanol, a small amount of the latter is oxidized to cyclohexanone, a factor which leads to slightly high results for cyclohexanone. The addition of acetic anhydride and urotropine (hexamethylenetetramine) prevents this process. Metabisulfite, acetic anhydride, and urotropine do not affect the coupling of the diazonium salt of H-acid with cyclohexanone.

Cyclohexanol was determined on the basis of the reaction with diphenylamine. On heating a solution of cyclohexanol in the presence of diphenylamine in a sulfuric acid medium at temperatures higher than 100°, a red color develops. The composition of the colored compound has not been established. The color of the solution does not conform to Beer's law (Fig. 1). Maximum light absorption is observed at 530 mμ (Fig. 2). The reaction sensitivity is 5 γ/ml.

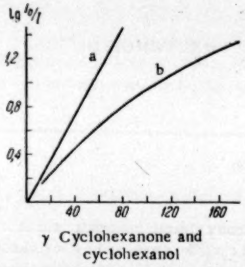


Fig. 1. Conformation of solutions to Beer's law:
a) Relation between optical density and cyclohexanone concentration during its reaction with the diazonium salt of H-acid; b) ditto for cyclohexanol during its reaction with diphenylamine.

Cyclohexanone in amounts up to 0.5 mg/ml does not give a color with diphenylamine on heating in a sulfuric acid solution. Higher concentrations of cyclohexanone give weak colors. Addition of hydroxylamine sulfate to the solution prevents formation of a color in the presence of cyclohexanone. The addition of hydroxylamine sulfate to the test solution does not have any appreciable effect on the reaction between cyclohexanol and diphenylamine.

Determination of Cyclohexanone

Reagents. 1. A standard aqueous solution of cyclohexanone containing 40 γ/ml.

2. A freshly prepared solution of diazotized H-acid. This is prepared by mixing equal volumes of a 1% solution of sodium nitrite, and a 0.25% solution of the mono-sodium salt of H-acid in 0.05 N sulfuric acid.

3. Acetic anhydride.

4. A 10% solution of urotropine.

5. A freshly prepared 1% solution of sodium metabisulfite.

6. A 25% solution of sodium hydroxide.

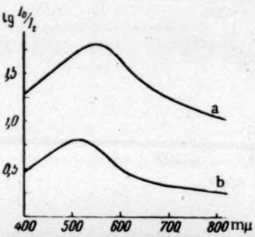


Fig. 2. Absorption curves:
a) Light absorption by solutions obtained during the reaction of cyclohexanone with the diazonium salt of H-acid. Cyclohexanone concentration 10 γ/ml; b) ditto for cyclohexanol during its reaction with diphenylamine. Cyclohexanol concentration 25 γ/ml of solution.

Analytical procedure. To 1 ml of test solution contained in a colorimeter tube is added 0.2 ml of urotropine solution and a drop (0.02 ml) of acetic anhydride. After mixing, 0.2 ml of the sodium metabisulfite solution and 0.2 ml of the sodium hydroxide solution are added, followed by 0.5 ml of the diazo salt of H-acid. After 5 minutes the solution is diluted accurately to the mark with water and the color intensity measured. A calibration curve for use in the photocolorimetric determination of cyclohexanone is constructed by taking various amounts of the standard solution of cyclohexanone in a series of colorimeter tubes. After the volumes in the tubes have been made equal by addition of water, the reagents are added, the volumes made up to 10 ml with water, and the color intensity measured on a photocolorimeter using a green filter.

Cyclohexanone can also be determined on the basis of its reaction with the diazonium salt of H-acid by the technique of colorimetric titration with a standard aqueous solution of the azo dye. In this case, into the control sample, after it has been diluted with water to 10 ml, is added dropwise from a microburet, a standard aqueous solution of the azo dye, until the color is the same as that of the test solution; the cyclohexanone content of the sample is then calculated from the amount of the azo solution added. 7.58 γ of azo dye is equivalent to 0.98 γ of cyclohexanone.

The azo dye required for the preparation of the standard solution to be used for the determination of cyclohexanone by colorimetric titration can be prepared by the procedure given below. To 100 ml of a 2% suspension of the monosodium salt of H-acid in 0.1 N hydrochloric or sulfuric acid is added dropwise 5 ml of a 10% solution of sodium

TABLE 1

Determination of Cyclohexanone in the Presence of Cyclohexanol by means of the Reaction with the Diazonium Salt of H-Acid

Taken		Cyclohexanone found, γ	Error, %
cyclohexanone, γ	cyclohexanol, mg		
1,0	—	1,09	+9,0
2,0	0,2	1,94	—3,0
—	0,3	0,00	0,0
4,0	0,3	3,75	—6,2
5,0	0,5	5,25	+5,0
7,0	0,5	7,6	+8,5
8,0	0,6	8,2	+2,5
10,0	1,0	9,65	—3,5
12,0	1,0	12,6	+5,0
15,0	1,5	14,7	—2 0
18,0	1,5	17,5	—2,7
20,0	2,0	21,2	+6,0
22,0	2,0	22,8	+3,6
25,0	2,5	24,2	—3,2
28,0	2,5	28,0	0,0
30,0	3,0	31,3	+4,3
32,0	3,0	32,4	+1,2
34,0	3,5	33,6	—1,1
35,0	3,5	37,0	+5,7
40,0	4,0	39,5	—1,3

TABLE 2

Determination of Cyclohexanol in the Presence of Cyclohexanone by means of the Reaction with Diphenylamine

Taken		Cyclohexanol found, in γ	Error, in %
cyclohexanol, in γ	cyclohexanone in mg		
10,0	0,10	11,2	+12,0
15,0	0,20	13,4	—10,6
20,0	0,30	18,4	— 8,0
—	0,50	0,0	— 0,0
25,0	0,50	26,2	+ 4,8
30,0	0,80	28,1	— 6,3
—	1,0	0,0	0,0
35,0	1,0	36,3	+ 3,7
40,0	1,0	38,2	— 4,5
45,0	1,5	41,5	— 8,7
50,0	1,5	53,5	+ 7,0
55,0	1,5	54,2	— 1,4
60,0	1,5	56,4	— 6,0
65,0	2,0	69,3	+ 6,6
—	2,0	0,0	0,0
70,0	2,0	66,1	— 5,6
75,0	2,0	78,8	+ 4,6
80,0	—	85,0	+ 6,3
90,0	2,0	92,8	+ 3,1
100	2,5	97,8	— 2,2

nitrite. The suspension of the H-acid, after addition of sodium nitrite, at first dissolves, but a yellow precipitate of the diazonium salt then separates out. After 5 minutes, 500 mg of cyclohexanone and 25 ml of an alkali mixture consisting of equal parts of 20% solutions of sodium sulfite and sodium hydroxide, are added to the reaction mixture. After addition of the alkali mixture, the precipitate of diazonium salt and H-acid dissolves, and the solution acquires an intense cherry-red color. After 20 minutes, 50% sulfuric acid is added dropwise to the solution until the color changes from cherry-red to brown, and until a precipitate is formed. Solution and precipitate are transferred to a No. 3 sintered funnel on which the solution is sucked off; the precipitate is washed three times with alcohol and dried in a drying oven at 105°. The yield is about 2 g.

Results of determinations of cyclohexanone in the presence of cyclohexanol are given in Table 1.

Determination of Cyclohexanol

Reagents: 1. A standard aqueous solution of cyclohexanol containing 100 γ / ml.

2. A 2% solution of diphenylamine in concentrated sulfuric acid.

3. A 25% aqueous solution of hydroxylamine sulfate.

Analytical procedure. To 2 ml of the test solution of cyclohexanol contained in a colorimeter tube is added 2 ml of the solution of diphenylamine in sulfuric acid. A standard scale is prepared at the same time. For the latter purpose various amounts of the standard solution of cyclohexanol, ranging from 10 to 100 γ, are introduced into a series of colorimeter tubes. When the volume in each tube has been adjusted to 2 ml, 2 ml of the diphenylamine solution is added to each of them. When the cyclohexanone content of the test material has been found to be greater than 1 mg, then 0.2 ml of the hydroxylamine sulfate solution is also added to each of the tubes. The colorimeter tubes forming the scale, and the tube containing test solution, are placed for 15 minutes in an oil bath kept at a temperature of 145-150°. After 15 minutes, the tubes are removed from the oil bath, wiped with cotton wool or paper, and the color intensity measured. Results for the determination of cyclohexanol by the reaction with diphenylamine are given in Table 2.

For the determination of cyclohexanone and cyclohexanol in air, water can be used as the sorbent. The air to be tested is drawn through three wash bottles, connected in series; each bottle contains water, and the and the air is drawn through them for one hour at the rate of 15-20 liters per hour. At the end of this time, 1 ml of liquid is taken from each wash bottle for determination of cyclohexanone, and 2 ml for the determination of cyclohexanol; analysis is then carried out by the methods described above. Usually, 70-80% of the cyclohexanone and about 90% of the cyclohexanol is trapped in the first wash bottle; in the second 20-30% of cyclohexanone, and about 10% of cyclohexanol is trapped. There is only a very insignificant break-through of cyclohexanone into the third wash bottle, when the concentration of cyclohexanone in air is higher than 20 γ/liter.

SUMMARY

A photometric method has been developed for the determination of cyclohexanone which is based on its reaction with the diazonium salt of H-acid; this technique permits determination of cyclohexanone in the presence of 100 times its amount of cyclohexanol. The sensitivity of the method is 0.2 γ/ml. Experimental error does not exceed 9% for cyclohexanone concentrations within the limits 1 to 40 γ in the test material.

A method has been developed for the determination of cyclohexanol by means of diphenylamine, which permits determination of cyclohexanol in the presence of 30 times its amount of cyclohexanone. The experimental error over the range 10 to 100 γ does not exceed 12%. The sensitivity of the method is 5 γ/ml.

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DETERMINATION OF PRIMARY, SECONDARY, AND TERTIARY AMINO GROUPS IN EACH OTHERS PRESENCE

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During a study of the nitrogenous compounds found in petroleum we developed a method for the determination of primary, secondary, and tertiary amino groups in each others presence. This method can be successfully applied to the analysis of mixtures of aliphatic and aromatic amines. The methods most widely used for the determination of primary amino groups are those of Van-Slyke, and diazometric titration with sodium nitrite of a solution of an aromatic amine in a strong mineral acid medium. One of the essential drawbacks of these methods is their inapplicability to the analysis of mixtures containing secondary amino groups. Tertiary amino groups can be determined in the presence of primary and secondary amino groups, when the primary and secondary amino groups are either destroyed beforehand by HNO_2 [1-2], or are acetylated by acetic anhydride [3].

In 1947 Wagner, Brown, and Peters [4] suggested an acidimetric method for the separate determination of primary, secondary, and tertiary aliphatic amino groups in each others presence. A little later, Siggia, Hanna, and Kewenski [5] extended this method to mixtures of aromatic amines.

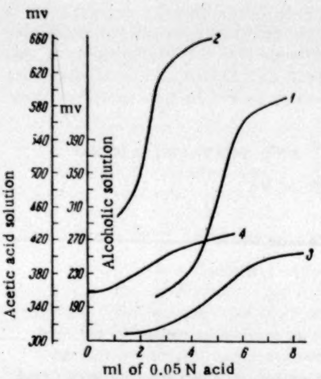
Their method consists of the following stages: first the total amino group content in the mixture is determined; in a second aliquot, the primary amino groups are then blocked by combination with salicylaldehyde $RNH_2 + OHC \cdot C_6H_4OH \rightarrow RN = CH \cdot C_6H_4OH + H_2O$. The Schiff bases which are thereby formed are weak bases which do not interfere with total acidimetric titration of secondary and tertiary amino groups. In a third aliquot of the sample the primary and secondary amino groups are acetylated with acetic anhydride, and the tertiary amino group, which remains unchanged, is then titrated. Knowing the total amino group content, the sum of the secondary and tertiary amino groups, and the tertiary amino content, it is easy to calculate the content of primary and secondary amino groups.

In the papers cited, the amino groups were determined either by titration in the presence of an indicator, or by potentiometric titration. The solvents used were isopropanol [4], and a mixture of isopropanol and ethylene glycol [5]; the titrants used were solutions of $HClO_4$ or HCl in the same solvents. The essential drawback of this method is the difficulty associated with determining the endpoint, arising from the fact that the alcohols used by the authors as solvents (isopropanol and ethylene glycol) are differentiating solvents with weakly expressed protogenic properties. Accordingly, the strength of the bases in these alcohols is only insignificantly higher than that in aqueous solutions. In practice, it is only possible to titrate those bases whose ionization constants are not less than $10^{-7} - 10^{-8}$.

After treatment of the mixture with salicylaldehyde the sensitivity of the reaction is lowered further, since salicylaldehyde always contains salicylic acid as an impurity, and this interferes with the titration.

Furthermore, the Schiff bases formed are titratable — though only to a small extent — in alcoholic solution.

In recent years, it has been shown in a series of papers [6-8], that glacial acetic acid is the best solvent for the acidimetric titration of amines. Amines are titrated very distinctly in a medium of glacial acetic acid. Amines whose ionization constants are of the order of $10^{-11} - 10^{-12}$ can be titrated in this solvent.



Titration curves for mixture IV (Table 2). 1) Titration of the mixture with $HClO_4$ in CH_3COOH; 2) titration of the mixture with $HClO_4$ after preliminary treatment with salicylaldehyde; 3) titration of mixture with HCl in isopropanol – ethylene glycol; 4) titration of the mixture with HCl after preliminary treatment with salicylaldehyde.

Nevertheless, the Schiff bases formed during the interaction of primary amines with salicylaldehyde are equal in strength to secondary and tertiary amines. As a result, during titration in glacial acetic acid of a mixture of amines containing Schiff bases, and secondary and tertiary amines, the total of amino groups is determined. The potentiometric titration curve in such cases has only one break.

In order to make it possible to carry out a differential determination of primary, secondary, and tertiary amino groups in a glacial acetic acid medium, we used phthalic anhydride instead of salicylaldehyde for quantitative blocking of the primary amino groups. Phthalic anhydride reacts with primary amines in glacial acetic acid to form the corresponding phthalimides. The latter, under the given conditions, behave as neutral substances, and, in contrast to the Schiff bases, do not interfere at all with subsequent titration of secondary and tertiary amines. The suitability of phthalic anhydride for the quantitative blocking of primary amino groups has been checked on a number of individual amines, and on mixtures of amines containing, in addition to primary amino groups, secondary and tertiary amino groups (Tables 1 and 2).

The results we obtained showed that phthalic anhydride can be successfully used for the quantitative blocking of primary amino groups in the presence of secondary and tertiary amino groups. The definition and accuracy of titration of the residual secondary and tertiary amino groups does not suffer at all under these conditions; the potential jump at the endpoint has almost the same value as for a solution of amines in glacial acetic acid in the absence of phthalimides.

Potentiometric titration curves are shown in the diagram for titration of mixture IV (Table 2), after treatment of this mixture with salicylaldehyde (Curve 4), and with phthalic anhydride (Curve 2). While the potential jump in the case of titration of amines in an alcoholic medium only amounts to 30-40 millivolts, in a glacial acetic acid medium this jump is 70-100 millivolts, i.e., the sensitivity of potentiometric titration more than doubles. As the results given in Tables 1 and 2 show, the method suggested proved to be fully suitable for the quantitative determination of primary amino groups in a number of aliphatic amines (determinations 1-6), aromatic amines (determinations 7-12), and for 3-aminopyridine and 3-aminoquinoline. The absolute experimental error, as a rule, is not more than 0.1% for a nitrogen content greater than 10%.

It should be pointed out that in the series pyridine, quinoline, and thiazole, the amino group in positions 2 and 4 possesses properties which are more amide-like than amino. During titration of 2- and 4-aminopyridines and aminoquinolines in glacial acetic acid with $HClO_4$, it is the monoperchlorates not the diperchlorates that are formed. Amino groups located in positions 2 and 4 do not react with either phthalic anhydride or acetic anhydride, and, accordingly, cannot be determined by this method. 2-Aminothiazole behaves in the same way. The amino group located in position 3 in the pyridine and quinoline ring reacts with phthalic anhydride, and can be titrated with $HClO_4$ in glacial acetic acid, i.e., it possesses basic properties. Thus, where 2- and 4-aminopyridines and quinolines are present in a mixture, the primary amino groups in these compounds cannot be determined by the method suggested (determinations 13, 14, 16, and 18 in Table 1). Tertiary amines were determined in the presence of primary and secondary amines by blocking the latter with acetic anhydride and titrating the residual tertiary amine in solution [9].

Experimental Procedure. Redistilled glacial acetic acid was used as the solvent.

Titration was carried out using 0.05 or 0.1 N $HClO_4$ in glacial acetic acid. The standard acid solution

TABLE 1

Acidimetric Determination of Primary Amines in Glacial Acetic Acid by Means of Phthalic Anhydride

Expt. No.	Test compound	Calculated, in %				N Found, in %	
		N_{total}	NH_2	NH	N	N_{total}	N after treatment with phthalic anhydride
1	Butylamine	19.15	19.15	–	–	19.23	0
						19.17	0
2	Amylamine	16.07	16.07	–	–	16.15	0
						16.15	
3	Isopropylamine	23.70	23.70	–	–	23.50	0
						23.51	
4	Di-n-amylamine	8.91	–	8.91	–	8.80	8.80
						8.85	8.88
5	Di-n-butylamine	10.84	–	10.84	–	10.74	10.77
						10.63	10.70
6	Methyloctadecylamine	4.94	–	4.94	–	5.01	4.95
						5.04	–
7	Aniline	15.05	15.05	–	–	15.07	0
						15.01	0
8	p-Toluidine	13.07	13.07	–	–	13.07	0
						13.07	0
9	o-Toluidine	13.07	13.07	–	–	12.98	0
						13.05	0
10	p-Anisidine	11.38	11.38	–	–	11.42	0
						11.42	0
11	p-Aminophenol	11.19	11.19	–	–	11.14	0
						11.13	0
12	n,n',p,p'-Diaminodiphenyldisulfide	11.28	11.28	–	–	11.33	0
						11.35	0
13	2-Aminopyridine	29.77	14.88	–	14.88	14.76	14.82
						14.80	14.83
14	4-Aminopyridine	29.77	14.88	–	14.88	14.68	14.65
						14.65	14.60
15	3-Aminopyridine	29.77	14.88	–	14.88	29.52	14.70
						29.62	14.65
16	2-Aminoquinoline	19.43	9.71	–	9.71	9.63	9.72
						9.68	9.63
17	6-Methoxy-3-amino-quinoline	14.72	7.36	–	7.36	14.62	7.38
						14.65	7.34
18	2-Aminothiazole	27.97	13.98	–	13.98	13.90	13.92
						13.81	13.93

was prepared from aqueous $HClO_4$ (40 or 70%) and glacial acetic acid, the water introduced being removed by addition of the calculated amount of acetic anhydride. The normality of this solution was established by titrating against a solution of potassium hydrogen phthalate in glacial acetic acid. Perchloric acid can be replaced by p-toluenesulfonic acid, which, in glacial acetic acid, behaves like a very strong acid [10]. It is essential to ensure that the temperature of the titrant does not change during titration. A LP-5 tube potentiometer was used for carrying out potentiometric titration. Titration was carried out with the aid of a glass stirrer connected to an electric motor.

An aliquot of test sample, the amount taken being dependent on the nitrogen content, is transferred to a

TABLE 2

Acidimetric Determination of Primary, Secondary, and Tertiary Amino Groups in Mixtures of Amines by Means of Phthalic Anhydride

No. of mixture	Amine mixture	Weight of sample in 100 ml of solution	Amount HCl used for titrating 25 ml of solution, ml			Calculated, in %				Found, in %			
			$N_{original \cdot total}$	total NH + N•	N••	N_{total}	NH_2^-	NH	N	N_{total}	NH_2	NH	N
1	Isopropylamine	0.1186	17.07	0	—	20.70	20.70	0	0	20.81	20.81	—	—
	Butylamine	0.0519	17.06	0	—					20.79	20.79	—	—
	Amylamine	0.0593											
2	Amylamine	0.0353	4.96	1.06	—	13.01	9.57	3.44	—	13.10	9.57	3.53	—
	Di-n-amyl-												—
	amine	0.0410	4.93	1.02	—					13.03	9.63	3.40	—
	Aniline	0.0297											
3	Aniline	0.0287	5.41	1.90	1.91	18.12	11.83•••	—	6.29	18.10	11.62	—	6.38
	p-Toluidine	0.0199	5.45	—	1.89					18.15	11.84	—	6.31
	2-Aminopyridine	0.0356											
4	Aniline	0.0489	5.03	2.36	0.92	13.67	7.18	3.84	2.65	13.75	7.29	3.95	2.51
	Methylanine	0.0301	5.05	2.33	0.97					13.80	7.41	3.73	2.66
	Dimethylaniline	0.0235											
5	Butylamine	0.0457	4.98	1.81	0.65	13.80	8.74	3.13	1.93	13.92	8.86	3.24	1.82
	Dibutylamine	0.0289	4.98	1.81	0.67					13.92	8.86	3.18	1.88
	Tributylamine	0.0255											

•After treatment of the solution with phthalic anhydride.

••After treatment of the solution with acetic anhydride.

•••Without taking into account the NH_2 group of 2-aminopyridine which is not titrated.

standard flask and made up to the mark with glacial acetic acid. An aliquot part of this solution (20-25 ml) is taken for each determination. Total amino nitrogen is determined on one part of the solution. To the second 20-25 ml lot of solution is added 1 g of phthalic anhydride (a two or threefold excess of the anhydride is taken with respect to the NH_2 groups); the solution is then heated under reflux on a boiling water bath for 30-45 minutes. The solution is cooled and the total secondary and tertiary amino groups remaining in solution determined by titration. To a third portion of solution is added 10-15 ml of acetic anhydride, and the mixture is heated under reflux on a boiling water bath for 30-45 minutes. The solution is cooled and the tertiary amino groups titrated. Knowing the total amino nitrogen, the sum of the secondary and tertiary amino groups, and the amount of tertiary amino groups, the content of primary and secondary amino nitrogen is calculated.

SUMMARY

A method is suggested for the acidimetric (potentiometric) determination of primary, secondary, and tertiary amino groups in a glacial acetic acid medium. The method is based on the quantitative blocking of primary amino groups with phthalic anhydride, and the blocking of primary and secondary amino groups with acetic anhydride. The use of acetic acid as solvent increases the potential jump at the end-point, and permits titration of nitrogen bases with dissociation constants of the order of $10^{-11} - 10^{-12}$.

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POLAROGRAPHIC DETERMINATION OF ALKYLNITRITES

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In recent years the problem of devising a reliable method for the quantitative determination of alkylnitrites (RONO) has become a real one. This is a consequence of the fact that according to modern concepts, alkylnitrites are formed as intermediates during nitration of paraffin hydrocarbons, probably according to the scheme:

$$\dot{R} + NO_2 \rightarrow RONO \tag{1}$$

At the moment of its formation in this way the nitrite molecule, however, carries excess energy amounting to about 57 kilocalories/mole, since the energy of formation of the bond R − ONO is equal to this amount [1]. A nitrite molecule as rich in energy as this is characterized by extreme instability, since the dissociation energy of the adjacent bond RO−NO is only 37 kilocalories/molecule [2]. As a result it can be assumed that a nitrite molecule formed according to reaction (1), will immediately break down, and will give rise to the formation of an alkoxy radical and nitric oxide:

$$RONO \rightarrow R\dot{O} + NO. \tag{2}$$

The alkoxy radical will undergo a series of further transformations, most of which will lead to the formation of oxygen-containing (without nitrogen) products, which are actually found during nitration of paraffins:

$$R\dot{O} \rightarrow R + HCHO; \tag{3}$$

$$R\dot{O} + RH \rightarrow ROH + \dot{R}. \tag{4}$$

In addition to reactions (3) and (4), the alkoxy radical can undergo one further transformation. As nitric oxide accumulates in the course of reaction (2) the probability of the reaction

$$RO + NO \rightarrow RONO, \tag{5}$$

will increase; this reaction proceeds almost without any activation energy, since it is a recombination of two free radicals. Since the thermal effect of reaction (5) is 37 kilocalories/molecule [2], the nitrite molecule which is formed may be stable and remain without further decomposition.

Thus, if alkylnitrites are found in the nitration products of paraffins, these alkylnitrites should be regarded as products of secondary origin.

The polarographic method appeared to us to be the most promising method for the determination of the small amount of alkylnitrites found in the complex mixture of nitration products of paraffins, Bliumberg and Pikaeva [3] have found that ethylnitrite in aqueous solutions can be reduced electrolytically on a dropping mercury electrode at a half-wave potential of −0.96 volt; the latter is independent of the pH of the medium.

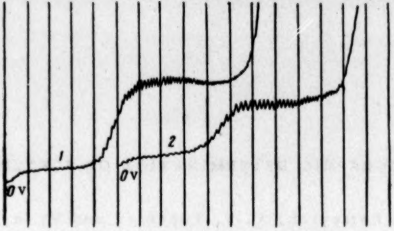

Fig. 1. Polarograms for ethyl- and butylnitrite in aqueous LiCl solutions:
1) Ethylnitrite in 0.1 N aqueous LiCl (ethylnitrite concentration 0.0386 wt. %); pH 2.5; 1 : 200; 20°; 2) butylnitrite in 0.1 N aqueous LiCl solution (butylnitrite concentration 0.013 wt. %); pH 2.9; 1 : 100; 20°.

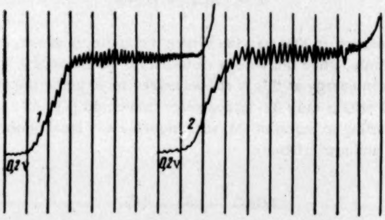

Fig. 2. Polarograms for ethyl- and butylnitrite in aqueous LiOH solutions.
1) Ethylnitrite in 0.1 N aqueous LiOH (ethylnitrite concentration 0.0284 wt. %); pH 12.2; 1 : 200; 20°;
2) butylnitrite in 0.1 N aqueous LiOH (butylnitrite concentration 0.09 wt. %); pH 12.3; 1 : 200; 20°.

These facts were used by the authors mentioned for the determination of ethylnitrite in the products formed by the interaction of ether with nitrogen peroxide in the gaseous phase [4].

We have also developed a polarographic method for the determination of alkylnitrites, taking ethylnitrite and butylnitrite as test materials.

The ethylnitrite was prepared by the action of concentrated hydrochloric acid on a mixture of an aqueous solution of $NaNO_2$ and ethanol [5]. The ethylnitrite thus prepared was dried over potassium hydroxide and distilled. The distilled product boiled at 17°.

Butylnitrite was prepared by pouring a mixture of sulfuric acid and butanol into an aqueous $NaNO_2$ solution [6]. After the mixture had separated into layers and the butylnitrite fraction had been removed, it was distilled under vacuum [24-27° (43 mm)]. The butylnitrite prepared had n_D^{20} 1.3770 (published value n_D^{20} 1.3773).

Solutions of the alkyinitrites prepared by dissolving aliquots of the nitrites, taken in glass ampoules, were subjected to polarographic study. In the case of ethylnitrite, the glass ampoule was cooled with solid carbon dioxide while it was being filled.

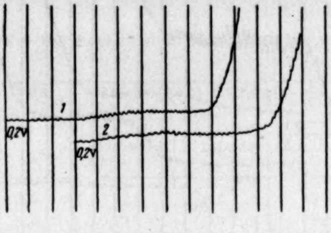

Fig. 3. Polarograms for aqueous solutions of ethyl- and butylnitrites in LiOH solutions: 1) An aqueous solution of ethylnitrite (ethylnitrite concentration 0.0574 wt. %) was mixed with an equal volume of 0.1 N aqueous LiOH; pH 11.8; 1 : 200; 20°; 2) an aqueous solution of butylnitrite (butylnitrite concentration 0.18 wt. %) was mixed with an equal volume of 0.1 N aqueous LiOH; pH 11.85; 1 : 200; 20°.

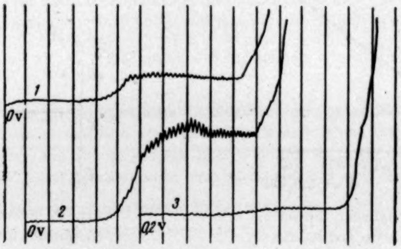

Fig. 4. Polarograms for aqueous $NaNO_2$ solutions at various pH values: 1) $NaNO_2$ in 0.1 N aqueous LiCl ($NaNO_2$ concentration 0.175 wt. %) plus 2 drops of HCl; pH 3.6; 1 : 500; 20°; 2) ditto plus another 2 drops of HCl; pH 3.0; 1 : 500; 20°; 3) ditto plus 0.2 N aqueous LiOH (1 : 1); pH 12.15; 1 : 200; 20°.

Oxygen dissolved in the electrolytes, was removed with a nitrogen stream before dissolving the alkylnitrites in them. Such a precaution is necessary because of the volatility of the alkylnitrites, particularly ethylnitrite.

Polarograms were taken on a polarograph made by the "Geologorazvedka" factory; the current–voltage curves were registered photographically.

The reduction potentials were measured relative to the saturated calomel electrode. The capillary used for making all measurements had the following characteristics $m^{2/3} t^{1/6} = 2.86\ mg^{2/3}\ sec^{-1/2}$; the pH of the solutions was measured on a LP-5 potentiometer with a glass electrode. The pH values adduced are uncorrected values.

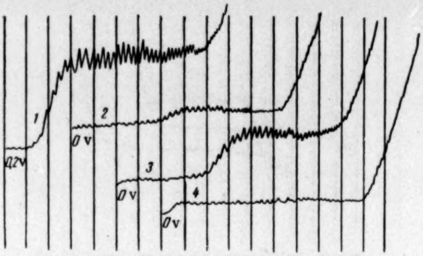

Fig. 5. Polarograms for butylnitrite in various media: 1) Butylnitrite in 0.1 N aqueous LiOH (butylnitrite concentration of 0.09 wt. %); pH 12.35;1 : 200; 20°; 2) ditto plus HCl; pH 3.9; 1 : 200; 20°; 3) ditto plus some more HCl; pH 3.2; 1 : 200; 20°; 4) ditto plus concentrated LiOH solution; pH 12.35; 1 : 200; 20°.

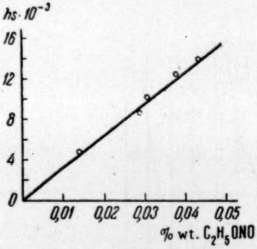

Fig. 6. Relation between the wave height for ethylnitrite and its concentrations in 0.1 N aqueous LiOH: pH 12.2; 20°.
h) wave-height, in mm; S) sensitivity.

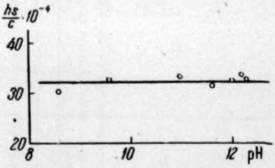

Fig. 7. Relation between the wave height of ethylnitrite and pH of the medium (LiCl + LiOH).
h) wave-height, in mm; S) sensitivity; c) concentration of ethylnitrite in wt. %.

Even the first experiments were sufficient to show that during polarographic determination of alkylnitrites is impossible to dissolve them in water or in aqueous solutions of electrolytes having a neutral or acid reaction. Under these conditions the alkylnitrites hydrolyze almost immediately to form alcohols and nitrous acid: $RONO + H_2O \rightarrow ROH + HNO_2$ (6). When this occurs there is a significant increase in the pH of the solution. For example, on dissolving $0.76 \cdot 10^{-3}$ g·mole of ethylnitrite in 100 ml of water, a solution with a pH of 2.7 was obtained, while on dissolving $1.02 \cdot 10^{-3}$ g·mole of ethylnitrite in 100 ml of a 0.1 N aqueous solution of LiCl a solution with a pH of 2.4 was obtained. The same was observed in the case of butylnitrite.

When polarograms were taken of solutions prepared in this way, there was observed quite a clear cut reduction wave for some compound at a half-wave potential of $\pi_{1/2} = -0.95$ volt. The only possible compound is nitrous acid, and, in fact, according to published results [7], the half-wave potential of this acid $\pi_{1/2} = -0.95$ volt (see also Curve 1, Fig. 4).

TABLE 1

Relation Between the Wave Height of Ethylnitrite and the Time it is in Contact with the Solution (LiOH)

Concentration of ethylnitrite in 0.1 N LiOH, in wt. %	pH of the solution	Wave height of ethylnitrite $hS \cdot 10^{-3}$* when polarograms were taken after:				
		0 minutes	15 minutes	45 minutes	60 minutes	24 hours
0.04315	12.5	14	14	13	13	7
0.0356	8.6	10.8	10	9.8	9.4	–

•h) wave height, in mm; S) sensitivity.

Hydrolysis of alkylnitrites in aqueous alkali media is slowed down strongly. Actually, the pH of alkali solutions did not decrease on addition of alkylnitrites. Thus, on dissolving $0.6 \cdot 10^{-3}$ g-mole of ethylnitrite in 100 ml of 0.1 N aqueous LiOH (pH 12.2), the alkalinity of the solution obtained remained the same (pH 12.2). If the ethylnitrite had hydrolyzed, the pH of the solution would have been 11.9.

Ethylnitrite and butylnitrite dissolved in 0.2 or 0.1 N aqueous LiOH, are reduced at a half-wave potential of $\pi_{1/2} = -0.65$ volt (Fig. 2).

Final confirmation of the fact that taking polarograms of acid solutions of alkylnitrites is equivalent to electro-reduction of nitrous acid ($\pi_{1/2} = -0.95$ volt), and that electro-reduction of the alkylnitrites themselves is only possible in alkaline media ($\pi_{1/2} = -0.65$ volt), was obtained in subsequent experiments, the results of which are shown in Fig. 3.

It is shown in Fig. 3 that when alkylnitrites were dissolved in water (when this was done an acid solution was obtained which gave a wave for nitrous acid when polarograms were taken, see Fig. 1), and then mixed with LiOH, the solution became alkaline and then gave some other reduction wave (in addition to that for Li). Curve 3 in Fig. 4 shows that a nitrous acid solution which has been made alkaline does not give a reduction wave either.

Figure 5 demonstrates the behavior of butylnitrite in various media. Curve 1, Fig. 5 with a nitrite wave ($\pi_{1/2} = -0.65$ volt) was obtained when polarograms were taken of its alkaline solution in LiOH (pH 12.35). When this solution was acidified to a pH of 3.9 then, as is evident from Curve 2, the wave of the nitrite itself disappeared, since it hydrolyzed, and instead of it there appeared the wave for nitrous acid ($\pi_{1/2} = -0.95$ volt). Further acidification to a pH of 3.2 led, as Curve 3 shows, to an increase in the wave height of the nitrous acid.• Finally, it is clear from Curve 4 (Fig. 5), that when the solution was again made alkaline to a pH of 12.35 neither a wave with $\pi_{1/2} = -0.65$ volt, was observed since the nitrite had already decomposed, nor was a wave with $\pi_{1/2} = -0.95$ volt observed, since nitrous acid does not exist in an alkaline medium.

At pH 12.3 the wave height for ethylnitrite remained almost constant for one hour (Table 1). After 24 hours it dropped to half its original value.

There is a linear relation between the wave height and concentration of ethylnitrite (Fig. 6).

•This increase could be the result of either a relation between the wave height of the reduction of nitrous acid and pH, or by the fact that, as some authors have suggested [8], in solutions of nitrous acid, it is not the nitrous acid itself which is reduced on the dropping mercury electrode, but nitric oxide molecules which are formed during decomposition of nitrous acid. In the latter instance, an increase in the acidity of the solution should lead to an increase in the amount of nitric oxide formed, accordingly there should be an increase in wave height. The first two curves (Fig. 4) obtained with a known solution of nitrous acid demonstrate that such an increase in wavelength is obtained whatever the explanation.

In order to study the relation between the wave height of ethylnitrite and the pH in the alkaline region, mixtures of aqueous solutions of LiOH and LiCl were prepared with pH 6.95; 8.6; 9.6; 11.0; 11.6; 12.0; 12.2; 12.3. Dissolution of aliquots of ethylnitrite in these mixtures had almost no effect on their pH values, with the exception of the mixture with pH 6.95. Polarograms obtained for solutions prepared in this way are shown in Fig. 7. As these results show, the wave height of ethylnitrite is almost independent of pH in the alkaline region.

The wave height of ethylnitrite in a supporting electrolyte of 0.1 N LiOH increases by 1.4-1.6% for 1° rise in temperature.

It should be noted that Bliumberg and Pikaeva [3], presumably assumed that the nitrous acid wave was the alkylnitrite wave. In those cases, where they worked with solutions of ethylnitrite in water or in aqueous LiCl, they undoubtedly were dealing with nitrous acid solutions. More difficult to understand is the appearance of a wave with $\pi_{1/2} = -0.95$ volt in an aqueous solution of ethylnitrite in LiOH as supporting electrolyte. Since, however, the authors did not indicate either the concentration of the ethylnitrite or the pH of the medium, the possibility arises that the amount of ethylnitrite they dissolved in water was such that when the acid solution thus obtained was mixed with 0.1 N LiOH, the medium continued to be acid.

Where, therefore, the polarographic method is used for determining alkylnitrites in the products obtained by nitration of paraffins or their derivatives, it is quite possible to arrive at a completely wrong result if the amount of alkylnitrite is assessed on the basis of the amount of nitrous acid obtained during hydrolysis of the alkylnitrite. It must be borne in mind that samples of the nitration mixture taken for analysis may always contain nitrous acid itself, as well as nitric oxide, which on dissolving in water also yields nitrous acid.

SUMMARY

1. It has been shown that alkylnitrites can only be determined polarographically in aqueous solutions when the pH is greater than 7.

2. The half-wave potentials of ethyl- and butylnitrite in an alkaline medium (in LiOH solutions0 have been shown to be −0.65 volt.

3. It has been shown that there is a proportionality between the height of the polarographic wave of ethylnitrite and its concentration in solution.

4. It has been demonstrated that the wave height of ethylnitrite in the alkaline region is almost independent of pH (from pH 8.6 to 12.3).

5. The wave height for ethylnitrite increases by 1.4-1.6% for a temperature rise of 1° of the solution.

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**In Russian.

PHYSICOCHEMICAL METHODS OF DETERMINING ANTIBIOTICS

COMMUNICATION IV. COLORIMETRIC DETERMINATION OF BIOMYCIN*

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The Russian preparation "biomycin" contains as active material an antibiotic which is known abroad as aureomycin or chlortetracycline.** Several quantitative methods have been described in the literature for the determination of chlortetracycline: fluorometric [1-4], spectrophotometric [5-6], and colorimetric [1, 2]. The simplest and most convenient for wide application in factory and research laboratories is the colorimetric method first suggested by Levine [1]. This method is based on the conversion of chlortetracycline, by heating in a hydrochloric acid solution, into anhydrochlortetracycline, which possesses an intense yellow-orange color [7].

Levine suggested the following operational procedure for the colorimetric determination of chlortetracycline. One ml aliquots of an aqueous solution of chlortetracycline is introduced into two standard flasks. To the first flask is added 5 ml of 2 N HCl, while 5 ml of distilled water is introduced into the second flask. Both flasks are immersed for 5 minutes in a boiling water bath, after which they are immediately transferred into cold water. Five ml of 2 N HCl is added to the second flask, and the volumes of both solutions made up to the mark with water.

The extinction of the first solution is then determined using the second as a background. For brevity we shall call this first solution the "colored" solution, while the second is called the "control." When a light filter with maximum transmission at 440 mμ is used, the extinction is directly proportional to chlortetracycline concentration.

In his paper, Levine [1] said nothing about the applicability of the method he suggested for determining the content of chlortetracycline in culture liquid, and for its determination during the intermediate stages under production conditions. The study of this important practical problem is the subject of the present article.

EXPERIMENTAL

All extinction measurements were made on a Hilger photoelectric colorimeter fitted with a filter having maximum transmission at 430 mμ. Of the light filters at our disposal we got maximum extinction with this filter.

Tests showed that maximum extinction is observed after standing the test solution in a water bath for 3.5 minutes. Longer heating leads to partial decomposition of the anhydrochlortetracycline formed.

The color of the cooled solutions hardly changes at all in the course of 5 hours; after 24 hours the drop $\Delta\epsilon$ only amounts to 5% ($\Delta\epsilon$ is the difference between the extinction of the "colored" and "control" solutions).

Some chlortetracycline compounds (Ca salts, etc.) dissolve only in dilute hydrochloric acid. Under such conditions, partial conversion of chlortetracycline into anhydrochlortetracycline is possible in the "control" solution, and this leads to a drop in the value of $\Delta\epsilon$; in order to prevent this, solutions with pH less than 1.9 should not be used.

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*For part III, see J. Anal. Chem. 12, 262 (1957). (1)

**For the rest of this article we shall use the term most commonly used at the moment—chlortetracycline.

TABLE 1

Results of Microbiological and Colorimetric Methods of Determining Chlortetracycline During its Inactivation in Acid Media at 30°

Time, in hours	pH 0.58		pH 2.00	
	microbiological determination, γ/ml	colorimetric determination, γ/ml	microbiological determination, γ/ml	colorimetric determination, γ/ml
0	200	223	494	500
22.5	115	115	–	–
24	–	–	440	492
73.5	–	–	330	490
76	54	30	–	–
99.5	9	14	–	–
312	–	–	117	463

TABLE 2

Results of Microbiological and Colorimetric Methods of Determining Chlortetracycline During its Inactivation in Alkaline Media at 30°

Time, in hours	pH 7.40		pH 8.78	
	microbiological determination, γ/ml	colorimetric determination, γ/ml	microbiological determination, γ/ml	colorimetric determination, γ/ml
0	400	422	530	460
2	–	–	115	123
4	–	–	40	37
25	110	152	–	–
29	–	–	5	13
123.5	7	12.5	–	–

For determination of very dilute solutions of chlortetracycline the amount of solution used for analysis can be increased (for example 5 ml instead of 1 ml). When this is done it is essential to keep the hydrochloric acid concentration a constant during the stage involving conversion of chlortetracycline into anhydrochlortetracycline.

Our experiments established that there is linear relation between $\Delta\epsilon$ and chlortetracycline concentration in the original solution, within the concentration limits for chlortetracycline (the base) below 1200-1300 γ/ml ($\Delta\epsilon = 0.3$).

The main reason for using the colorimetric method of determining the antibiotic is to replace the microbiological method which takes a long time to carry out.

Tests have shown that the colorimetric and microbiological methods give results which are in good agreement with each other for culture liquids, starting at chlortetracycline contents of 50γ/ml. At lower concentrations, the colorimetric method gives appreciably lower results.

In aqueous solution, chlortetracycline undergoes changes, the nature and rate of which depend on the pH of the medium and on temperature.

A detailed study of the kinetics of these processes does not come within the scope of the present work. Results of experiments on the determination of chlortetracycline after storing it in solutions at various pH values are given in Tables 1 and 2.

TABLE 3

Number of Milliliters of 0.006 N $K_2Cr_2O_7$ Solution Required for Preparing Standards

Standard No.	Vol. of 0.006 N solution, ml	A	Standard No.	Vol. of 0.006 N solution, ml	A	Standard No.	Vol. of 0.006 N solution, ml	A	Standard No.	Vol. of 0.006 N solution, ml	A
0	0,0	0	6	11,4	150	11	30,3	400	17	58,8	800
1	1,9	25	7	15,2	200	12	34,5	450	18	66,7	900
2	3,8	50	8	18,9	250	13	38,5	500	19	76,9	1000
3	5,7	75	9	22,7	300	14	41,7	550	20	90,9	1200
4	7,6	100	10	26,3	350	15	45,5	600	21	100,0	1300
5	9,4	125				16	52,6	700			

TABLE 4

Determination of Chlortetracycline Concentrations by the Visual and Microbiological Methods

Solution, containing chlortetracycline	Microbiological method, γ/ml	Visual method, γ/ml
Culture liquid	66	86
" "	140	146
" "	120	112
Butanol solution	155	187
Solution of the Ca salt of chlortetracycline in 0.02 N HCl	450	440
Imported aureomycin	1260	1140

It is clear from the results given in Tables 1 and 2 that a sharp discrepancy between the two methods is observed only in a solution with a pH about 2. At lower pH values, and in the weakly alkaline region the results of both methods almost coincide.

Changes which the molecule of chlortetracycline undergoes and which have been described in the literature [7], permit the following explanation to be given for these results. All the compounds which are formed by some change or other in the molecule of chlortetracycline are either biologically inactive, or are considerably less active than the original compound. In the presence of high hydrogen ion concentrations the main change is formation of anhydrochlortetracycline. During the colorimetric determination of chlortetracycline which has partially changed into anhydrochlortetracycline, the difference in the extinction between the "colored" and "control" solutions will, naturally, be determined only by the chlortetracycline which has remained unchanged, since the color inherent in the anhydro-form in both solutions is mutually compensated. From this, it is quite comprehensible that there should be agreement between the results of the colorimetric and microbiological methods of determination.

In weakly acid solutions, the basic process is, presumably, the conversion of chlortetracycline into epichlortetracycline [8], which is biologically inactive, but still does not loose its capacity to give a colored anhydro-form. This explains the sharp difference between the biological and colorimetric methods during the inactivation of chlortetracycline in weakly acid media.

Inactivation of chlortetracycline in alkaline media is caused by its conversion into isochlortetracycline [7], which is biologically inactive, and is incapable of forming an anhydro-form.

A visual method involving standards for determining chlortetracycline concentration. When no photoelectric colorimeter is available, chlortetracycline concentrations can be established by means of a selection of standards. A very suitable material for preparing standards is a solution of potassium dichromate, since such solutions are very similar in color to those of anhydrochlortetracycline (0.2942 g of chemically pure $K_2Cr_2O_7$ in 1 liter of solution). A series of standards can be prepared by introducing the amounts of 0.006 N potassium dichromate solution indicated in Table 3 into 100 ml standard flasks, and making the volume to the mark with distilled water.

The series of standards prepared in this way are poured into ampoules 60-70 mm long and 25-28 mm in diameter, and the ampoules sealed. For establishing the chlortetracycline concentration, all the operations indicated above are carried out, taking 1 ml of test solution and finally making up the volume to 50 ml. Both "colored" and "control" solutions prepared in this way are poured into ampoules, whose dimensions are exactly the same as those containing the potassium dichromate standards. From the series of standards (see Table 3) ampoules are chosen whose solutions correspond in intensity to the "colored" and "control" solutions. This operation is best carried out on a background of mat or frosted glass, an electric lamp being placed on the other side of the glass. To each number of the standard there corresponds a definite ciphered value A, chosen so that the difference between them gives directly the chlortetracycline concentration in the original test solution. Thus, if the "colored" solution corresponds to standard No. 14 (A-550), while the "control" solution corresponds to standard No. 4 (A-100), then the concentration of the chlortetracycline will be 550−100= 450 γ/ml. When the test solution is very dilute, then it is necessary to take more than 1 ml of solution. In such a case the value obtained according to column A should be divided by the number of milliliters of solution taken.

During determination of the chlortetracycline content of solutions free from other colored impurities, the use of a "control" solution is not obligatory, since the intensity of its color always amounts to a definite fraction of the intensity of the "colored" solution. In this case it is sufficient to multiply the value of A corresponding to the value of the "colored" solution, by the coefficient 0.96 and to obtain the concentration of chlortetracycline in γ/ml. For technical preparations, and, particularly, for culture liquids it is necessary to choose standards for both the "colored" and the "control" solutions.

The visual method described has been applied several times for the rapid determination of chlortetracycline concentrations under production conditions, and gave completely reliable orienting results.

Table 4 contains results obtained by this method. Taking into account the accuracy of the visual method, and the unavoidable errors of the biological method, the agreement between the results obtained by the two methods can be regarded as satisfactory.

The colorimetric method of determining chlortetracycline which we have studied possesses a high specificity, and is distinguished by this feature from many other colorimetric methods of determining antibiotics. Thus, in order to determine streptomycin and mannozidostreptomycin it is necessary to separate them quantitatively beforehand in a more or less pure form by means of ion exchange resins. On the other hand, colorimetric determination of chlortetracycline can be carried out directly in culture liquids despite the presence of appreciable amounts of impurities contained in such liquids.

SUMMARY

1. More accurate conditions have been established for the quantitative determination of chlortetracycline (biomycin); the method is based on conversion of chlortetracycline into anhydrochlortetracycline, followed by colorimetric determination of the latter (Levine's method).

2. It has been shown that this method is very specific and permits determination of chlortetracycline, not only in pure and commercial samples, but during intermediate stages in the production of the antibiotic. The method is also suitable for culture liquids as long as their chlortetracycline content is not less than 50 γ/ml.

3. A visual, semi-quantitative, colorimetric method has been developed for the determination of chlortetracycline, using standard solutions of potassium dichromate of varying concentrations as reference standards.

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BRIEF COMMUNICATIONS

A PHOTOMETRIC METHOD FOR THE DETERMINATION OF COBALT AS COBALTINITRITE

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In acetic acid solutions, in the presence of sodium nitrite, cobaltinitrite is formed and this is often used for the precipitation of potassium. The intense color of solutions of the sodium salt has not hitherto been used for determination of cobalt.

Alongside other studies being carried out at the moment in the Chemical Institute of the Jassy Branch of the Rumanian Social Democratic Academy of Sciences on the use of sodium nitrite in chemical analysis [1, 2], we have carried out some work in order to develop a photometric determination of cobalt in the form of sodium cobaltinitrite.

TABLE 1

Co^{2+}, in ml	Co^{2+}, in mg	$D - \lg I_0/I$			Co^{2+}, in ml	Co^{2+}, in mg	$D - \lg I_0/I$		
0,10	0,05	0,100	0,105	0,105	1,00	0,50	0,385	0,385	0,385
0,20	0,10	0,130	0,130	0,130	1,25	0,625	0,450	0,450	0,45
0,30	0,15	0,180	0,180	0,180	1,50	0,75	0,525	0,520	0,520
0,40	0,20	0,195	0,195	0,200	1,75	0,875	0,590	0,590	0,590
0,50	0,25	0,230	0,225	0,225	2,00	1,00	0,650	0,645	0,650
0,60	0,30	0,270	0,265	0,265	2,25	1,125	0,720	0,715	0,715
0,70	0,35	0,310	0,310	0,310	2,50	1,25	0,770	0,770	0,775
0,75	0,375	0,320	0,325	0,320	2,75	1,375	0,850	0,850	0,855
0,90	0,45	0,365	0,360	0,365	3,00	1,50	0,895	0,890	0,900

The stock solution of cobalt nitrate contained 0.5 mg of Co^{2+}. To various amounts of this solution contained in 25.0 ml standard flasks were added 2.0 ml lots of glacial acetic acid, and 5.0 ml lots of a solution obtained by dissolving on heating, 120 g of chemically pure sodium nitrite (free from potassium nitrite) in 180 ml of twice-distilled water; by means of a capillary whose tip was bent into the shape of an L, air was passed into the solutions for 10-15 minutes in order to remove the nitrogen oxides formed, the volume of the solutions was then made up to the mark* with water; colorimetric measurements were then made, distilled water being used as the reference, the cells were 10.0 mm, while a blue filter was used in a FEK-M photocolorimeter. Results obtained in this way are given in Table 1.

When measurements are made relative to sodium nitrite solution (5.0 mg in 25 ml of water) instead of water, the solutions have a smaller optical density (Table 2).

A calibration curve was constructed on the basis of the experimental results (Table 1). The results conform to Beer's law for concentration greater than 0.35 mg Co/ml. For smaller amounts of cobalt, the optical density is less than that expected.

There are no changes in the optical density of sodium cobaltinitrite solutions in the course of 2 hours.

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*The pH of the solutions obtained in this way was 3.9 ± 0.1 (glass electrode).

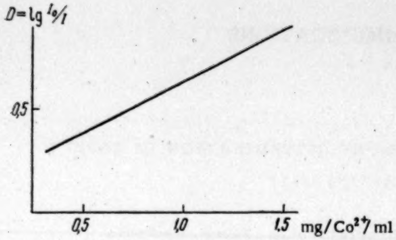

TABLE 2

Co^{2+}, in ml	Co^{2+}, in mg	$D = \log I_0/I$		
0.5	0.25	0.165	0.160	0.165
1.0	0.50	0.320	0.320	0.315
1.5	0.75	0.450	0.450	–
2.0	1.00	0.580	0.580	0.575
2.5	1.25	0.700	0.700	0.710
3.0	1.50	0.820	0.815	0.815

The optical density remains almost constant on decreasing the amount of sodium nitrite added to 3 ml; on decreasing the amount to less than 3 ml, the optical density drops sharply.

Changes in glacial acetic acid concentration within the wide limits of 0.5-2 ml have almost no effect on the final optical density of the solutions.

Potassium and ammonium ions, even in trace amounts, can lead to the formation of precipitates and to a decrease in the optical density of the solution.

Cupric ions give an intensely green colored solution which complicates determination of cobalt. The yellow color of VO_3^- ions is superimposed on the color developed from cobalt. Bismuth interferes by giving a yellow color.

Cr^{3+} ions, in the presence of sodium nitrite and acetic acid impart a weak rose color to the solution; 1.0 mg of Cr^{3+} has almost no effect on the optical density. Divalent tin in amounts less than 2.0 mg does not interfere; when larger amounts of tin are present, a gelatinous precipitate is formed.

Fe^{3+} ions interfere strongly with cobalt determination. Determination of 0.5 mg of Co^{2+} in the presence of 1.0 mg of Fe^{3+} is only possible when sodium fluoride is added beforehand to the test solution, the same procedure as before is then followed; after the solution has been made up to the mark, it is filtered through a filter paper (blue band) and the optical density measured rapidly so as to prevent damage to the cell.

In the presence of large amounts of iron the optical density of the solutions is abnormally high.

Determination of 0.5 mg of Co^{2+} is also possible in the presence of 10.0 mg Pb^{2+} or Sb^V, 20 mg of Zn^{2+}, Cd^{2+}, or Mn^{2+}, or 24 mg of Ni^{2+}.

It is possible to determine 0.5 mg of Co^{2+} in the presence of 100 times its amount of sexivalent uranium.

SUMMARY

It has been established that small amounts of cobalt can be determined photometrically in the form of sodium cobaltinitrite.

Solutions conform to Beer's law within the range 0.35-1.50 mg Co^{2+}/ml.

Large amounts of UO_2^{2+} ions do not interfere with cobalt determination.

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CONDUCTOMETRIC DETERMINATION OF CARBONATES AND BICARBONATES IN EACH OTHERS PRESENCE

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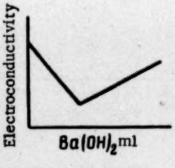
Conductometric titration of carbon dioxide and its salts has been described by Kolthoff [1] who indicated that during such titrations inaccurate results are obtained.

In order to establish the equivalence point more accurately we have developed the following method. Hydrochloric acid is added to the test solution containing carbonates in order to liberate carbon dioxide; residual hydrochloric acid is titrated with alkali. From the amount of residual acid (determined on the basis of the first break on the curve) it is possible to calculate the amount of carbonates present in solution.



Conductometric titration of hydrochloric and acetic acids with barium hydroxide.

During determination of hard water carbonate it is expedient to add a small amount of acetic acid to the test solution before titration, the purpose of the acetic acid is to prevent possible deposition of certain ions as their carbonates or hydroxides. During titration of a test solution containing carbonates, to which both hydrochloric acid and acetic acid have been added, residual hydrochloric acid is titrated first; this is followed by titration of the acetic acid. The amount of carbonate present is determined from the first break; there is no need to carry titration of acetic acid to completion, it is sufficient to get a enough points for constructing the second branch of the curve. The titration curve exhibits an acute angle (Fig. 1), which permits determination of the equivalence point with reasonable accuracy.

The procedure adopted is as follows: into the vessel to be used for conductometric titration [2] is introduced a measured volume (5 ml) of 0.01 N hydrochloric acid, followed by acetic acid (5 ml of 0.01 N), and distilled water to make the volume up to 25 ml. The solution is stirred and then titrated conductometrically with barium hydroxide whose strength is about 0.1 N. The reagent is added from a microburet.* The amount of barium hydroxide used for titrating the volume of hydrochloric acid taken is thus determined. Determination of carbonate and bicarbonate in test solutions is then carried out.

For the conductometric titration of sodium carbonate and bicarbonate in acid solutions as well as in the presence of foreign salts by means of barium hydroxide, the titration solution was prepared as follows. Five ml of the standard hydrochloric acid solution was measured into the conductometric titration vessel, followed by a known volume of a standard solution of sodium carbonate or bicarbonate, and 5 ml of 0.01 N acetic acid. The solution was made up to 25 ml with distilled water, stirred, and then titrated with barium hydroxide.

When titration was carried out in the presence of a foreign salt, a known volume of a solution of this salt was added to the vessel before titration. Having determined the amount of barium hydroxide from the break on the curve, the amount of carbonate in mg-equivalents/ml was calculated.

Results obtained during the titration of pure solutions of carbonates are given in Table 1; these results show that titration by the method suggested can be carried out at concentrations of up to 0.002 mg-equivalents of carbonate in 25 ml of solution to be titrated.

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* Titration was carried out in an apparatus of the Toropov type [3].

TABLE 1

Conductometric Determination of Carbonate and Bicarbonate in Each Others Presence

Taken, in mg-equivalents			Found, in mg-equivalents	Error, in %
Na_2CO_3	$NaHCO_3$	$NaHCO_3 + Na_2CO_3$		
–	0,017100	0,017100	0,017201	0,59
0,010100	—	0,010100	0,010137	0,36
–	0,008550	0,008550	0,008549	0,02
0,005050	—	0,005050	0,005047	0,06
–	0,001710	0,001710	0,001545	0,66
0,001010	0,017100	0,018110	0,018231	0,67
0,002500	0,012825	0,015325	0,015450	0,81
0,005050	0,008550	0,013600	0,013699	0,72
0,007500	0,004275	0,011775	0,011845	0,59
0,010100	0,001710	0,011810	0,011845	0,24

TABLE 2

Determination of the Carbonate Hardness of Natural Waters

Sample No. of water	Carbonate hardness, in mg-equiv.		Volume of test water taken for analysis by the conductometric method, in ml
	by Khlopin's method	conductometrically	
1	2.82	2.86	5
2	3.38	3.40	5
3	5.20	5.27	2.5
4	6.98	7.00	2.5
5	12.30	12.36	2
6	23.63	23.89	1
7	26.18	26.30	0.5

In the case of smaller amounts of carbonate, large errors are obtained.

Calcium, magnesium, and aluminum ions do not interfere with titration of carbonate and bicarbonate. Incorrect results are obtained in the presence of iron; all the same, interference from iron can readily be eliminated by adding a small amount of dry sodium fluoride to the solution being titrated. Under these conditions the acetate complex of iron is broken down (the solution is decolorized) and the more stable complex between iron and sodium fluoride is formed.

Sulfate ions present in solution do not interfere as long as a small amount of dry barium sulfate is added to the solution prior to titration, as well as a solution of methyl violet,* and also a small amount of 1% barium chloride solution (from 0.5 to 2 ml depending on the sulfate ion concentrations of the test solution).

Phosphate ions interfere with the determination because they combine with the hydrogen ions of hydrochloric acid to form hydrophosphate ions. $H_2PO_4^-$ ions do not interfere, while both HPO_4^{2-} and PO_4^{3-} ions lead to completely erroneous results.

Interference from phosphate ions is removed by adding 5 ml of a 1% solution of barium chloride to a known volume of test solution, and, 1-2 minutes after the precipitate has settled out, filtering the solution through a small filter into the conductometric titration vessel. The beaker in which precipitation is effected is washed out three times with small portions of distilled water, and the washings poured through the filter.

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* Dry barium sulfate is added in order to improve crystallization conditions, while methyl violet is added in order to prevent adsorption of ions on the precipitate formed.

The filter is washed finally with distilled water and the filtrate obtained prepared for titration as indicated above.

The method developed has been used for the determination of hard water carbonate, the value of which is defined as the total amount of carbonate and bicarbonate in solution. For this purpose, a known volume of test water (from 0.5 to 5 ml) depending on its expected carbonate hardness is pipetted into the titration vessel, to the solution is added a small amount of dry barium sulfate, 5 drops of a saturated solution of methyl violet, 0.5 ml of 1% barium chloride solution, 5 ml of 0.01 N "standardized" hydrochloric acid, 5 ml of 0.01 N acetic acid, and the volume made up to 25 ml with distilled water. The solution is stirred, and titrated conductometrically with barium hydroxide. From this curve the amount of barium hydroxide used up is determined, and from this figure the carbonate hardness of the water is calculated in mg-equivalents/liter.

When the test water contains phosphates, they must be removed prior to titration by means of barium chloride as described above.

The carbonate hardness of a series of test waters was determined both by the suggested conductometric method, and by a method involving titration with 0.1 N hydrochloric acid using alizarin as indicator [4]. The results from both these methods are given in Table 2; they show that the conductometric method suggested can be used for determining carbonate hardness of test waters. The advantage of this method is the speed with which it can be carried out.

SUMMARY

A conductometric method has been developed for determining carbonates and bicarbonates; it is based on titration of excess hydrochloric acid added to the test solution by means of barium hydroxide. The method can be used for determining the carbonate hardness of water.

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CHRONICLE

CONFERENCE ON THE ANALYSIS OF GASES IN METALS

From the 24th to the 27th of June 1958 a conference was held in Moscow on the analysis of gases in metals, it was organized by the Commission on Analytical Chemistry of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR. About 200 representatives from scientific-research institutes, factory laboratories, and laboratories of higher education establishments, were present at the conference. Some Chinese scientists were also present: Professor Ts'u Iu-Ch'i, Tu T 'un (Institute of Ferrous Metals, Peking), Li Tieh-Fang (Institute of Metals, Acad. Sci. Chinese Democratic Republic, Shen 'lan).

In his introductory address, A. P. Vinogradov pointed out the importance of increasing the sensitivity of the methods used for determining gases in metals.

In Iu. A. Kliachko's report on the present position with regard to methods of determining gases in metals, it was pointed out that in order to choose a method for determination of gases in metals, it is essential to know in what form the gas is present in the metal (solution, chemical compound, adsorption or surface compound, mechanical inclusion).

At the conference reports were given dealing with the physicochemical bases of determination of gases in metals, with various methods of determining hydrogen, oxygen, and nitrogen, and with modern apparatus. Several reports were devoted to the vacuum-fusion method which has found wide application in recent years.

I. I. Kornilov read a report on results of studies of the diagram of state of the systems: Group IV elements – oxygen. The report of V. I. Fistual dealing with a mass-spectrographic method of determining the concentration of diffusion coefficients of gases in metals evoked considerable interest. The physicochemical principles of the determination of gases in metals by the vacuum-fusion method were considered in the report by L. L. Kunin and E. M. Chustiakova. A. M. Iakimova dealt in detail with the interaction of titanium with hydrogen. R. Sh. Khalitov communicated results of studies on the possibility of using the isotope dilution method for the determination of oxygen in titanium. The quantitative determination of oxygen in the lower oxides of titanium by x-ray analysis was the subject of the report by L. M. Kuznetsov, E. S. Makarov, and Z. M. Turovtseva. Great interest was evoked by the report of P. V. Gel'd and R. A. Riabov on the effect of alloy components (carbon, silicon, chromium, vanadium, manganese, and nickel) and of phase transformations on the rate of diffusion of hydrogen in steels at high temperatures.

Reports by B. A. Shmelev, Iu. A. Kliachko, and T. A. Izmanova, and by V. A. Zhabina and K. Ia. Shpunt dealt with the methods of vacuum-fusion and vacuum-heating. The use of a platinum bath for analyzing microsamples by the vacuum-fusion method formed the subject of the report by Z. M. Turovtseva, N. F. Litvinov, N. M. Vasil'ev, and K. G. Semeniuk. A new variant of the vacuum-fusion method for the determination of gases in the alkali metals was presented in the report given by N. F. Litvinov, B. I. Malyshev, and Z. M. Turovtseva. E. D. Malikova's communication touched on the application of the mercury extraction method for the determination of oxygen in the alkali metals. Z. M. Turovtseva reported on modern apparatus for determination of gases in metals by vacuum-fusion.

The report of A. N. Zaidel', A. A. Petrov, and K. I. Petrov was devoted to a method they have developed for the determination of hydrogen in metals by means of isotopic equilibrium, with subsequent spectroscopic determination of the isotopic composition of the equilibrium products in the gaseous phase. The use of the spectrographic-isotopic method for the determination of hydrogen in bronze and in various marks of steel was discussed in the report given by T. F. Ivanova, M. E. Trentovius, and V. V. Fedorov. A technique for the quantitative spectrographic determination of hydrogen in titanium alloys, steels, and welded joints was the subject of the report by E. S. Kudel' and O. P. Riabushko. The report of K. A. Sukhenko, N. S. Sventitskii, P. P. Galonov, and T. V. Barasheva also dealt with the spectrographic method of determining nitrogen in steels, and of determining hydrogen in titanium and its alloys.

A. N. Zaidel' and A. A. Petrov gave an interesting report on a new setup for the spectrographic-isotopic method for determination of hydrogen in metals. A lively discussion followed a report on an apparatus for spectrographic emission determination of gases in metals (A. A. Skotnikov and V. V. Dymov).

A special session was devoted to the use of chemical methods of analysis: the chloride-sulfuric and the sulfuric methods of determining oxygen in metals and oxides (K. E. Kleiner), determination of oxygen in the alkaline-earths by distillation (E. D. Malikov and Z. M. Turovtseva), and the thermo-fractionation method of determining nitrides in steels (M. S. Kovtun).

I. K. Zadorozhnyi dealt with the mass-spectrographic method of determining inert gases in iron. Special attention was given to a report on the radioactivation method for determination of oxygen in metal and semiconductors on the basis of the reaction $O^{16}/\gamma , n/O^{15}$ (A. Kh. Breger, B. F. Ormont, B. A. Chapyzhnikov, V. S. Kutsev, B. I. Viting, V. A. Kozlov, and L. V. Chapel'). Of equal interest was the report by L. F. Usova on the determination of gases in metals by the internal friction method. The sensitivity of the method amounts to 10^{-5}% (by weight).

Li Tieh-Fang of the Institute of Metals of the Academy of Sciences, Chinese Democratic Republic, dealt with the work of Chinese research workers on the determination of gases in metals.

The conference adopted a resolution to the effect that the papers presented should be published as soon as possible.

G. V. Mikhailova and N. F. Litvinova

BOOKS PUBLISHED BY THE USSR ACADEMY OF SCIENCES

"Akademkniga"

V. Ia. Anosov, "The Geometry of Chemical Diagrams" (transformation of coordinates in diagrams of binary systems) (The N. S. Kurnakov Institute of General and Inorganic Chemistry) Price 6 roubles 30 kopecks.

The book contains chemical diagrams of binary systems (alloys, solutions, etc.) widely used in various studies.

A. I. Busev and N. G. Polianskii, "The Use of Organic Reagents in Inorganic Analysis," (Review of literature published during 1953-1955). (Institute of Scientific Information. "Scientific Results" Series). Price 3 roubles.

A review of the most important papers on the theory and practice of organic reagents in inorganic analysis published during recent years in Russia and abroad.

G. I. Gess, "Thermochemical Research" ("Classical Science" series) Price 7 roubles.

V. I. Gol'danskii and E. M. Leikin, "Transformations of Atomic Nuclei" (Nuclear Reactions). (Popular science series). Price 6 roubles 60 kopecks.

The properties of atomic nuclei and elementary particles are characterized, and detailed descriptions are given of nuclear reactions which are used for producing atomic energy.

N. D Zelinskii (Academician) "Selected Works" (In four volumes), Vol. IV Price 34 roubles.

Papers on synthetic rubber and physical chemistry, and on research connected with development of a carbon gas mask, etc.

"Isotopes and Radiation in Chemistry", Transaction of the All-Union Scientific-Technical Conference on the Use of Radioactive and Stable Isotopes, and of Radiation in the Social Economy and Science (April 4-12, 1957). Price 18 roubles 20 kopecks.

Reports on the kinematics and mechanisms of chemical reactions on radiation chemistry, analytical chemistry,, physicochemical analysis, etc.

V. V. Lebedev. "Hydrogen, Its Production and Applications," (Popular Science series) Price 1 rouble 20 kopecks.

The book deals with the physical and chemical properties of hydrogen and its importance in nature and modern industrial techniques.

"Production of Isotopes, High-Power Gamma Setups, Radiometry, and Dosimetry," Transactions of the All-Union Scientific-Technical Conference on the Use of Radioactive and Stable Isotopes, and ofRadiation in the Social Economy and Science, April 4-12, 1957. (USSR Academy of Sciences. Main Administration on the Use of Atomic Energy of the USSR Soviet of Ministers). Price 14 roubles.

F. M. Perel'man, "Methods of Constructing Multicomponent Systems; Five-Component Systems," (The N. S. Kurnakov Institue of General and Inorganic Chemistry) Price 6 roubles.

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THE USE OF AN IMPULSE SOURCE FOR SPECTRA EXCITATION DURING THE SPECTROGRAPHIC ANALYSIS OF SILICATES

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Two basic approaches are known for the use of spectrographic methods in the analysis of silicate rocks. The first approach [1, 2] is to get the sample into solution and then analyze it by the usual methods; the second [3-5] is applicable to the analysis of solid rock powders, but requires that the test material be diluted several times with a buffer mixture. Sometimes, with the aim of increasing the accuracy of a determination, it is recommended that additional apparatus be used which stabilizes the operation of the spectra excitation sources, such as magnetic blowing [6], blowing the air along electrodes arranged vertically [7-9] etc. While these methods are characterized by operations which are tedious and difficult, the accuracy attained by their use is relatively low, and, according to the results given by various authors, are of the order of 4 — 7% and 6 — 10%. This factor limits, and sometimes, complicates the wide practical application of these methods.

High-temperature impulse sources of spectra excitation, as experiments carried out in our laboratory have shown, enable the accuracy of the spectrographic analysis of silicates to be increased.

Of a number of impulse sources which have been suggested in the last ten years [10-17], our attention was attracted to one suggested as long ago as 1945 by Levintov [10-13] for carrying out spectrographic determination of metalloids. Impulse intensification of the current of a stationary arc was realized by means of a periodic discharge from a high-voltage condenser through it. We used a high-temperature spectra excitation source of this type in the work described in the present article.

The excitation source is shown schematically in Fig. 1. The stationary element of the setup is a d.c. arc with carbon electrodes fed from a mercury rectifier (U_p = 270 volts); the impulse is supplied by a condensed spark from a IG-2 generator. The optimum operating conditions of the source were chosen experimentally in accordance with the results of work carried out by Sobolev [18 — 19] and Raiskii [20]. A minimum value of the inductance was chosen (L = O), while the capacity was 0.02 μF, and the value of the discharge gap was varied within the limits 0.5 to 3 mm. In order to protect the d.c. circuit from current impulses, use was made of a filter constructed from two symmetrically arranged self-inductances, with a total inductance of 120 μH and a capacity of 1 μF (U_{times} = 400 volts). As is evident from the schematic diagram, at the same time as the knife-switch 4 is switched on, during light contact of the electrodes with one another, a magnetic starter 5 comes into operation, the magnetic starter being connected into the d.c. circuit in parallel with an additional resistance 6. This leads to short-circuiting of terminals 7, through which a potential is applied to the inlet of the primary winding of the high-voltage transformer of the generator.

As a result of the superposition of a spark discharge on the arc, impulse intensification of the current occurs, the strength of which, according to preliminary measurements, amounts to 400 — 500 amps.

An impulse arc is characterized by a number of properties, which profitably distinguishes it from the usual type of d.c. arc. Thanks to this, the accuracy of spectrographic determinations is increased.

A simplified technique based on the application of the well-known Ornstein method [21-22] was used for establishing the temperature of the impulse arc. The method is applicable to sources in which, during a state

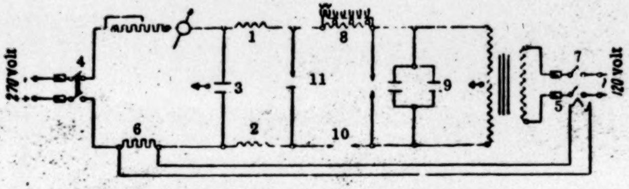

Fig. 1. Scheme of an impulse source of spectra excitation:
1-2) Inductance of the protective filter; 3) capacity of the protective filter; 4) knife-switch; 5) magnetic starter; 6) resistance; 7) terminals; 8) inductance of the spark generator, 9) capacity of the spark generator; 10) auxiliary discharge gap; 11) operating discharge gap.

of equilibrium, a Boltzmann distribution of the atoms and ions in the plasma holds good. In cases where the absolute values of the probabilities of transitions for various spectral lines are not known, this method can still be used to give an approximate idea of the temperature of the source by comparing it with other sources whose temperature is known. Determination of the temperature of the test source is carried out by means of the relation:

$$2{,}3\lg\frac{I_x}{I_s}=2{,}3\lg\frac{N_{0x}}{N_{0s}}+\frac{E}{K}\left(\frac{1}{T_s}-\frac{1}{T_x}\right).$$

where I_x and I_s are the intensities of the lines of an element, the energies of the upper levels (E) of which are known; T_x and T_s are the corresponding temperatures of the test and standard source; K is the Boltzman constant. This relationship is presented graphically within the coordinates $\log\frac{I_x}{I_s}-E$. The slope found in this way enables one to find the temperature T_x required, directly from the known value of T_s.

In order to measure the temperature of the impulse arc, its central part was reflected onto the slit of a spectrograph by means of a two-lens illumination system. The electrodes were covered with ZnO containing 0.3% Bi_2O_3. Measurements were carried out on the basis of the Bi I lines, the energies of whose upper levels are known from the work of Sobolev [19].* The temperature of the standard arc, operating in ZnO vapor was taken to be equal to 6100°K on the basis of Brinkman's work [23]. Both the d.c. arc and the impulse arc were operated at 10 amps. and 270 volts. The relationship established experimentally between logarithm $\frac{I_{Bi}\text{(impulse arc)}}{I_{Bi}\text{(arc)}}$ and E is shown in Fig. 2. From the slope of the straight line which was 0.58, it was found that the temperature of the impulse arc approximated 9800° K.

The extent of the changes in the line intensities along the interelectrode gap in the impulse arc and in the usual arc, for the lines Zn I 3075.9 and Zn II 2557.9 A, is shown in Fig. 3. In contrast to the usual arc, for which, in our experiments, there was observed a regular change in the intensity of the spectral lines of the ionized atoms on going from anode to cathode, and a characteristic intensification of the intensities in the region near the electrode, in the impulse arc, the intensity of these lines, just like the intensity of the lines developed during excitation of the atoms of the elements, remains almost constant along all the interelectrode gap. Spectrograms obtained under identical conditions, using an impulse arc and an ordinary d.c. arc, show that in the first instance, there occurs a significant increase in the total brightness of the spectra. Under such conditions, there is observed an increase in the number of lines of the ionized atoms and an increase in their intensity (see Table 1).

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* The temperature of a d.c. arc operating in NaCl vapor as measured by this method, proved to be 4600°K. This is in good agreement with the latest results of Kolesnikov and Pokhil'ko [24].

The high temperature of the source, the uniformity of the spatial distribution of the excited atoms and ions in its interelectrode gap, and some of the characteristics of the way in which the material passes into the active zone of the source* have a favorable effect on the reproducibility and accuracy of spectrographic determinations. During work with an impulse arc, the relative intensity of lines of different elements is considerably less than in a normal source, and depends on the extent of their homogeneity. One can readily be convinced of this, for example, by examining the curve shown in Fig. 4. Here is shown the relation between the difference in blackening of the lines Na 5889.9 (2.1 ev) and Cu 5700.2 A (3.82 ev) and changes, over a fairly wide range, in current strength and in the distance between electrodes in the impulse arc. A constant value for ΔS is not observed in an ordinary d.c. arc.

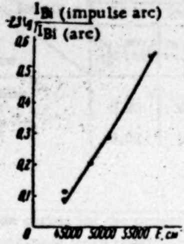

Fig. 2. Determination of the temperature of the impulse arc

A Technique for the Analysis of Silicates. A d.c. impulse arc permits one to extend the number of basic components of silicate rocks that can be determined simultaneously, to simplify analysis, and, what is most important, to increase its accuracy and reproducibility. The method described below has been designed with the object of carrying out a simultaneous quantitative determination, on one aliquot of test material, of nine basic components of rocks of different mineralogical and chemical composition, for contents of these components ranging from 0.5 to 80%. These elements include: Si, Ti, Al, Fe, Ca, Mg, Mn, Na, and K. Prior to analysis, with the object of removing absorbed water, the sample is dried for one hour at 105 – 110 deg. In order to reduce fractional evaporation of the elements to a minimum, the test material is diluted in the proportion of 1:1:2 with cupric oxide and carbon powder. The mixture obtained is carefully mixed for 10 – 15 minutes in an agate mortar, and then 30 mg of it placed in the anode cavity (3.5 × 4 mm). The cathode is a cylindrical carbon rod 2 mm in diameter. In order to prevent sputtering from the electrode cavity, the sample is moistened beforehand with two drops of distilled water and then dried. The spectra are excited by means of an impulse arc operating at 10 amps. and 270 volts. The IG-2 spark generator is controlled to operate according to a composite system at $L = 0$; $c = 0.02\ \mu F$ and an auxiliary spark gap of 0.5 mm. Under these conditions, 4 – 5 discharges of the condenser occur during the half-period of the current. The central part is projected by means of a three lens illumination system, through an intermediate diaphragm 2, onto the slit of the ISP-22 and ISP-51 spectrographs (the camera has a focal length of 270 mm). For convenience in carrying out photometric measurements, a two-stage attenuator is fitted in front of the spectrograph slits; exposure 1.5 minutes. During this time (see curves in Fig. 5) there occurs almost complete evaporation of the elements to be determined from the test sample. The spectra are registered on "Reproduction" plates with a sensitivity of 1.4 GOST units, and "Infrachrome 760" and plates developed in a D-19 developer.

The analytical lines of the elements, and the corresponding reference lines are given in Table 2. The Table also contains information on the concentration ranges of the elements to be determined, within which these lines can be used most expediently.

In order to construct calibration curves and to carry out control determinations, samples of silicate materials were chosen, the composition of which (Table 3) was established by classical chemical methods.**

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* The problem of the mechanism of the passage of test material from the electrode crater into the active zone of the impulse source, and the relation between arc and spark conditions of operation is of great practical and scientific interest; it has not been studied enough and is at present being investigated in our laboratory.

** The authors wish to thank N. V. Bulanov for his gift of several samples of "Martin" slags which had been analyzed.

TABLE 1

Spectral line in A / Source	Line blackening							
	Ionized atom				Non-ionized atom			
	Cu II 2837,5 (10,7 eV)	Zn II 2558,0 (10,95 eV)	Zn II 2502,0 (10,95 eV)	C II 2836,7 (16,3 eV)	Cu I 3247,5 (3,82 eV)	Zn I 3075,9 (4,03 eV)	Cu I 2441,6 (5,1 eV)	Zn I 3345,0 (7,78 eV)
Impulse arc	0,20	0,99	0,87	0,33	0,52	0,95	0,96	0,71
d. c. arc	0,02	0,39	0,21	0,05	0,54	0,92	1,01	0,73

Calibration curves for the quantitative determination of silicon, titanium, aluminum, iron, calcium, magnesium, and manganese were constructed on the basis of the blackening of the analytical lines with the coordinates ΔS — logarithm C. During determination of sodium and potassium, as noted already [25], it was found more expedient to use the method of the width of the spectral line.

TABLE 2

Lines of the test element, in A		Lines of the reference element in A		Optimum concentration range, in %
Si	2987,7	Cu	3030,8	10,0—80,0
Ti	3075,2	Cu	3010,8	0,10—2,50
	3186,5		3194,1	
Al	3944,0	Cu	3194,1	0,50—40,0
Fe	2950,2	Cu	3010,8	0,50—3,0
	3024,0		3010,8	3,0—40,0
Ca	3158,9	Cu	3194,1	0,50—9,0
	3180,5		3194,1	8,0—50,0
Mg	2776,7	Cu	3010,8	1,0—40,0
	2802,7		3010,8	0,01—2,0
Mn	2800,1	Cu	3010,8	0,01—1,0
	2933,1		3010,8	0,30—20,0
K	7664,9	Cu	7933,1	0,50—14 *
	7798,9		5218,2	
Na	5880,9	Cu	8092,6	0,50—12 *
	5895,9		5218,2	

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* Where necessary the upper concentration limit can be increased to 30%, while the lower limit can be dropped to 0,1%.

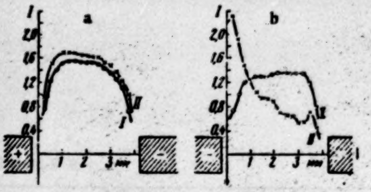

Fig. 3. Change in line intensity of excited atoms (1). and ions (2) along the interelectrode gap of the source for an impulse arc (a) and for a d. c. arc (b).

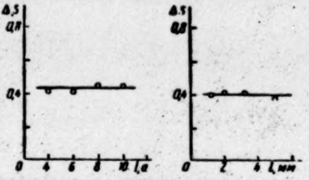

Fig. 4. Relation between the blackening differences of two lines, and changes in current strength, and the distance between electrodes in an impulse arc.

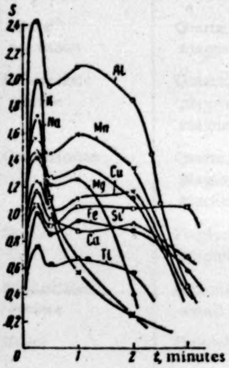

Fig. 5. Curves illustrating passage of elements into the active zone of the impulse arc.

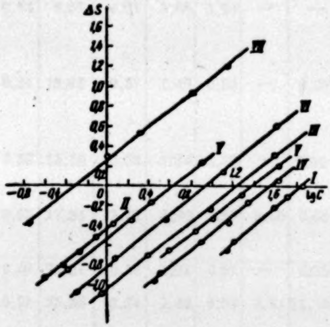

Fig. 6. Calibration curves for the determination of the oxides of: Si (I); Ti (II); Al (III); Fe (IV); Ca (Va, b); Mg (VI); Mn (VII) in rocks.

The appropriate curves are shown in Figs. 6 and 7.

Despite the considerable difference in the mineralogical and chemical composition of the samples tested, no mutual effect of the elements on one another could be detected, neither did the bulk composition have any effect on the results of the spectrographic determination. This can be explained, presumably, by the high temperature and the stability of the excitation conditions of the atoms in the source employed, and also by the uniformity of the distribution of the test elements in the interelectrode gap of the impulse arc.

The reproducibility of the method described was evaluated by comparing the results of determination of the contents of the test elements in a number of parallel experiments. In Fig. 8, for example, are given results for five parallel determinations of the contents of the main components, and the blackening differences of the lines relating to these experiments. Results obtained when an ordinary arc was used are given on the right, while the results on the left are those obtained by means of an impulse arc. The reproducibility of the results obtained by means of an impulse arc is almost twice as high as that obtained when using an ordinary arc. The mean arithmetic error (calculated on 5 replicates) varied within the limits 2 to 3%.

TABLE 3

Sample	Mineralogical composition	Chemical composition, in %								
		SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O
Clay	Kaolinite, monothermite quartz, rutile	48.90	2.00	33.02	2.28	0.36	0.25	0.03	—	0.07
Clay marl		32.78	0.38	8.76	3.68	15.30	10.99	—	1.88	1.76
Arkose sandstone	Quartz, feldspar, magnetite	72.44	0.53	9.56	6.97	1.66	1.24	—	—	2.49
Leucocratic granite	Quartz, orthoclase, plagioclase, biotite, magnetite	72.42	0.34	13.65	2.57	1.49	0.52	—	3.33	4.66
Granodiorite	Quartz, orthoclase, plagioclase, hornblende, biotite, magnetite	68.31	0.56	15.18	3.58	3.34	1.38	—	2.99	4.06
Diorite	Plagioclase, pyroxene, amphibole, orthoclase	56.06	0.65	17.31	7.76	6.92	3.60	0.15	2.65	2.59
Nephelinic syenite	Orthoclase, nepheline, alkali amphibole, biotite	57.23	0.46	20.51	2.56	1.68	0.66	—	2.32	12.44
Urtite	Orthoclase, pyroxene	51.08	0.21	25.46	3.64	1.43	0.99	0.11	11.10	3.94
Metamorphic shale	Quartz, bitotite, magnetite, granite	45.52	0.43	9.26	35.73	—	3.74	—	0.05	1.15
Granite	Quartz, orthoclase, plagioclase, biotite	70.90	0.20	12.98	1.90	2.94	0.45	0.09	6.37	0.58
Sham	Pyroxene, granite, quartz	48.14	0.10	0.87	23.6	22.88	0.92	2.41	—	—
Biotitic hornstone	Quartz, biotite, plagioclase, orthoclase	52.2	0.70	18.01	7.17	2.43	1.60	—	4.31	6.25
Quartz monzonite	Plagioclase, amphibole, orthoclase, quartz	63.57	0.42	15.75	4.19	4.77	1.92	0.10	5.02	1.99
Saxonite	Olivine, pyroxene	42.13	0.07	2.43	7.65	2.05	41.34	0.08	—	—
Dunite	Olivine, pyroxene	36.60	0.06	1.87	8.07	1.34	40.40	0.10	—	—
Martin slag		12.15	—	7.85	17.60	42.60	13.75	3.40	—	—
Martin slag		16.72	—	2.43	37.00	30.48	7.91	18.31	—	—
Coal ash		28.16	—	22.73	43.39	2.40	0.76	—	—	—

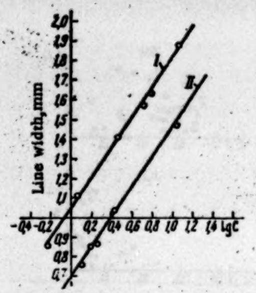

Fig. 7. Calibration curves for the determination of the oxides of: K (I) and Na (II) in rocks, by means of the spectral line width method.

The reliability of the method was checked by comparing the results of chemical and spectrographic determinations of the elements in 60 samples of rock. Some of the results obtained are shown graphically as examples in Fig. 9. The content of the element as determined chemically in the sample is plotted along the abscissa, while the relative values of the deviation of the results of spectrographic determination of the same elements using an ordinary arc 3 and an impulse arc, are plotted along the ordinate. As these results show, the use of an impulse arc permits one to achieve a significant increase in the accuracy of a determination. The maximum deviation between the results obtained by the spectrographic and chemical methods, did not exceed 4% for all the test elements. This error could be reduced by carrying out two-fold photometric measurements on the spectrograms.

As practice in the use of the techniques developed earlier [26, 27] has shown, an impulse source of spectra excitation can also prove useful for the quantitative spectrographic analysis of the main components not only of rocks, but also of other nonmetallic objects. In all these cases, the technique developed distinguished itself from the chemical methods for silicate analysis by the speed with which it can be carried out; it also requires incomparably smaller amounts of test material.

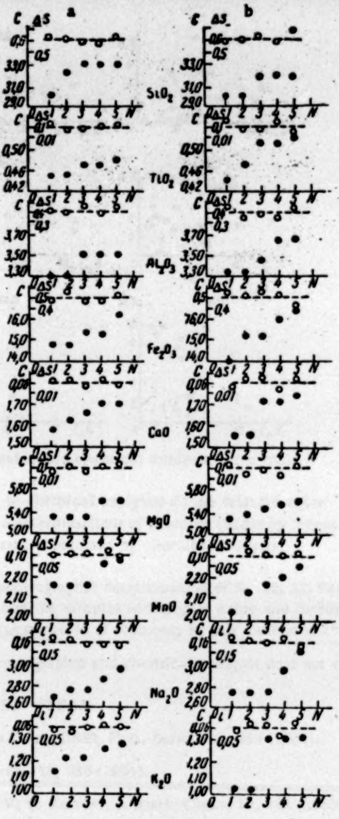

Fig. 8. Reproducibility of the results of spectrographic determination of elements in rocks using an impulse arc (a), and a d. c. arc (b): ●) content of element (C), in %; ○) blackening difference of the lines of the element and of the reference element (ΔS); N) number of experiments; e) line width.

SUMMARY

1. An attempt has been made to use an impulse source for carrying out spectrographic analysis of silicate rocks for their main components. The source described has an operating temperature of about 10,000°K, and is characterized by a considerably more uniform distribution of the excited atoms and ions in the plasma, than in the case of a d.c. arc. The relative intensity of the lines of various elements hardly depends at all on their degree of homology.

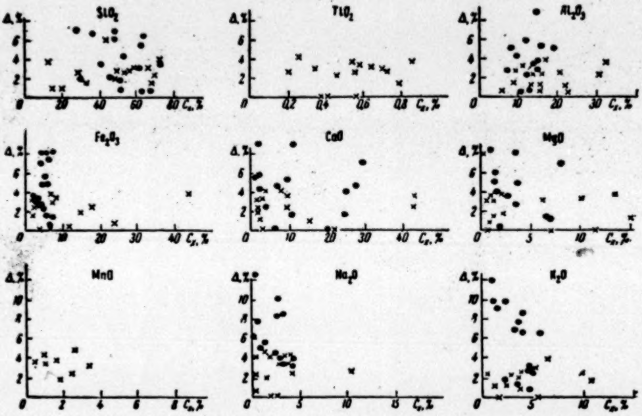

Fig. 9. Comparison of the results of spectrographic and chemical analysis of the main components of rocks:
C_x) the content of the metal oxides according to chemical analysis; Δ) the relative value of the deviation of the results of spectrographic determinations of element oxides by means of an impulse arc (+) and a d.c. arc (●), from results obtained by chemical analysis.

2. The technique developed for the quantitative spectrographic determination of Si, Ti, Al, Fe, Ca, Mg, Mn, Na, K in silicate rocks, does not require high dilution of the samples with cupric oxide and carbon powder for carrying it out. The mean arithmetic error for the determination of elements by this method is 2 – 3%.

The maximum deviation between the results of spectrographic and chemical analyses does not exceed 4%.

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THE MUTUAL EFFECT OF ELEMENTS ON RADIATION INTENSITY IN A FLAME

COMMUNICATION I. THE USE OF THE TWO-SPRAYER TECHNIQUE

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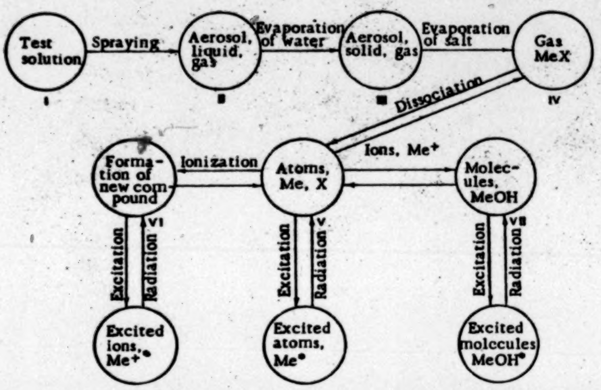
Flame photometry has acquired considerable importance in recent years [1]. Descriptions of various types of apparatus have been published in which the requisite radiation is isolated by both light filters and by spectroscopes – monochromators. Numerous methods have been developed for analyzing a very wide variety of test materials – rocks, water, and industrial and biological materials. The method has found wide application for the determination mainly of the alkali and alkaline-earth metals, and also for a number of other elements.

During the determination of various metals it has been observed on several occasions that the results obtained depend to a very large extent on the composition of the solution, and on the presence of various impurities in the solution. The effect of foreign materials has been studied several times, and, despite the fact that the reason for this interference has not always been made sufficiently clear, nevertheless, practical techniques have been devised whereby determinations have been carried out with the required degree of accuracy. The mechanism of the effect of foreign materials can differ and depends on the nature of the material added, excitation conditions, and the properties of the radiating element. Of primary importance is the fact that interference during the determination of one element on the basis of the intensity of its spectral lines in the presence of another element, can be caused by the superposition of the molecular bands of the second element on the radiation of the first; thus the molecular band of SrOH is superimposed on the lithium line at 670.8 mμ. Another type of interference is connected with insufficient selectivity of the filters, and the transmission by the filters of part of the radiation from the foreign metals (for example, the light filter designed for the determination of sodium on the basis of the resonance doublet 589.0 – 589.6 mμ, usually, partly transmits the molecular band of CaOH with a maximum at 622 mμ, etc.). Interference is caused in spectrophotometers by the fact that the light is not sufficiently monochromatic, and by the presence of scattered light. We shall not go into any further discussion of the effect of interferences arising from the apparatus, nor of the effects caused by the action of organic materials which change the viscosity and surface tension of solutions, thereby affecting the spraying process, but we shall concentrate on the mutual effect of inorganic materials.

The Mutual Effect of the Alkali Metals on the Radiation. Lundergardh, who was the first to develop in detail the technique of working with a flame, was of the opinion that the alkali metals have very little effect on the intensity of one another [2]. However, more detailed studies by Borovik-Romanova [3] on rubidium, showed that the intensity of the rubidium line at 780.0 mμ is depressed in the presence of the chlorides of sodium and potassium, and in the presence of the bromide and iodide of these metals, but does not change in the presence of sodium fluoride. We shall discuss the explanation given by Mandel'shtam [4] for this phenomenon during a description of the "anion effect"; Mandel'shtam explained it by a decrease in the percentage dissociation of rubidium chloride in the flame.

Ivanov [5] has also observed a drop in the intensity of the rubidium line, when sodium chloride is present at the same time as rubidium in solution, nevertheless, this decrease was only observed when illuminating gas


Test solution
Spraying
Aerosol, liquid, gas
Evaporation of water
Aerosol, solid, gas
Evaporation of salt
Gas MeX
I
II
III
IV
Dissociation
Formation of new compound
Ionization
Atoms, Me, X
Ions, Me⁺
Molecules, MeOH
VI
V
VII
Excitation
Radiation
Excitation
Radiation
Excitation
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Excited ions, Me⁺*
Excited atoms, Me*
Excited molecules MeOH*

Fig. 1. Schematic diagram of processes which occur during introduction of a solution of a metal salt, MeX, into a flame.

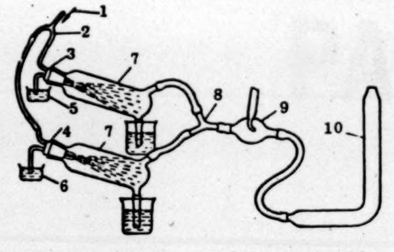
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Fig. 2. Schematic diagram of the setup used for introducing solutions into the flame by means of two sprayers:
1) Compressed air supply; 2) T-piece; 3 and 4) sprayers; 5 and 6) test solutions; 7) sprayer chamber; 8) T-piece; 9) mixer for introduction of fuel gas; 10) burner.

was used (T. F. Borovik-Romanova used an acetone vapor flame, the temperature of which is approximately the same as that of illuminating gas). In a flame from a mixture of acetylene and air he observed strengthening of the rubidium lines. A study of the mutual effect of the alkali metals on powdered silicic acid containing metal salts, which was introduced into a flame, led to the important conclusion that the increase in radiation intensity is greater, the higher the atomic weight of the element added, and also the higher the atomic weight of the radiating element when the same impurity is present. Similar observations and conclusions have been made by Putzmann [6]. Subsequently, the mutual increase in the radiation of the alkali metals — mainly sodium and potassium — has been observed on many occassions [7 — 12], and is, at present, explained on the basis of the ionization processes of the metal atoms in the flame.

According to this explanation, during ionization of the metal in the flame gases according to the equation

$$Me \rightleftarrows Me^{+} + e^{-} \; (e - \text{electron})$$

there exists an equilibrium between atoms, ions, and electrons:

$$\frac{P_{Me^{+}} \cdot P_{e^{-}}}{P_{Me}} = K$$

TABLE 1

Experiments Carried Out With Two Sprayers on Readily Ionizable Metals (air-acetylene flame)

Test element and its concentration in solution		λ in mμ	Element added, and its concentration, in γ/ml	Photocurrent value on addition of the foreign element into the flame (as a % of the photocurrent obtained in the absence of the foreign element)	
γ/ml	M			taken together	taken separately
Cs, 26.6	$2 \cdot 10^{-4}$	852	K 50	407	445
Cs, 26.6	$2 \cdot 10^{-4}$	852	K 100	617	622
Cs, 26.6	$2 \cdot 10^{-4}$	852	K 500	1416	1330
Cs, 26.6	$2 \cdot 10^{-4}$	852	K 1000	1520	1460
Cs, 50	$3.75 \cdot 10^{-4}$	852	K 1000	834	783
Cs, 100	$7.5 \cdot 10^{-4}$	852	K 1000	563	590
K, 3.9	10^{-4}	766 – 769	Cs 133	863	800
K, 9.8	$2.5 \cdot 10^{-4}$	766 – 769	Cs 133	469	483
K, 19.5	$5 \cdot 10^{-4}$	766 – 769	Cs 133	380	379
K, 39	$10 \cdot 10^{-4}$	766 – 769	Cs 133	253	253

(Saha's equation [13, 14] P_{Me}, P_{Me^+}, P_{e^-} are the partial pressures of the atoms, ions, and electrons).

On introducing another ionizing metal into the flame, the partial pressure P_{e^-} of the electrons increases, as a result of which the partial pressure of the ions should decrease, while P_{Me} should increase.

This assumption does, in fact, explain fairly well all the regularities involved in the mutual increase in intensity of the alkali metals in a flame, such as: the fact that the effect is observed to a greater extent in hotter flames and for metals which have low ionization potentials, the fact that the effect is observed to a greater extent at low concentrations, the fact that the greatest effect is observed on introducing readily ionizable metals (cesium), the fact that this increase in intensity of the radiation of a metal proceeds only to a certain limit, which corresponds to suppression of ionization, and, finally explains the linear relationship which exists between radiation intensity and concentration in the presence of another alkali metal.

The Anion Effect. The change in percentage dissociation of metal salts on introducing large amounts of salts of other metals, according to Mandel'shtam [4], is the reason for the drop in intensity of the radiation of the alkali metals. Dissociation of a metal halide according to the equation $MeX \rightleftharpoons Me + X$ (X — halide) should conform to the law of mass action:

$$\frac{P_{Me} \cdot P_X}{P_{MeX}} = K,$$

where P_{Me}, P_X, P_{MeX} are the partial pressures of the metal atoms, the halide, and the salt respectively. The addition of more atoms of halide which increases P_X should lead to a decrease in P_{Me}, and this, in turn, should lead to a drop in the intensity of the radiation of the element in the flame. In such cases, a similar effect should be exhibited not only by salts of the alkali metals, but also by acids and their ammonium salts. Experimental confirmation of this is to be found in [15]. Another possible explanation is the effect of acids or their salts on the evaporation of the solvent from drops of aerosol during its passage through the chamber of the sprayer; this affects the amount of material reaching the flame without deposition on the chamber walls [16].

The effect of acids depends on their nature and their concentration, and is most strongly expressed in the case of phosphoric acid. It has been established that with increasing phosphoric acid concentration up to a cer-

TABLE 2

Investigation of the Nature of the Anion Effect

Test element and its concentration in solution		λ in mμ	Material added and its concentration, M	Photocurrent value on addition of the foreign material as a % of the photocurrent for the solution without addition of foreign material			
				Acetylene flame		Illuminating gas flame	
γ/ml	M			taken together	taken separately	taken together	taken separately
Na, 23	10^{-3}	589—589.6	HCl, 0.1	97	102	96,5	97
Na, 23	10^{-3}	589—589.6	HCl, 1,0	92	97	96	99
Na, 23	10^{-3}	589—589.6	HCl, 2.0	83,5	88	85	96
Na, 23	10^{-3}	589—589.6	HCl, 5.0	65,5	81	55,5	81,5
Na, 50	$2{,}2 \cdot 10^{-3}$	589—589.6	HCl, 5,0	55	66	—	—
K, 50	$1 \cdot 3 \cdot 10^{-3}$	766—769	HCl, 2,0	85	85	—	—
K, 50	$1 \cdot 3 \cdot 10^{-3}$	766—769	HCl, 5,0	56	81	—	—
K, 50	$1 \cdot 3 \cdot 10^{-3}$	766—769	2,0	86	91	—	—
Ca, 50	$1{,}25 \cdot 10^{-3}$	422.7	HCl, 5,0	55	66	—	—
Na, 23	10^{-3}	589—589,6	NH_4Cl 1,0	84	90	78	87
Na, 23	10^{-3}	589—589,6	NH_4Cl 2,0	79	88	77	88
Na, 23	10^{-3}	589—589,6	NH_4Cl 5,0	55	75	55	78

TABLE 3

The Effect of Sulfuric and Phosphoric Acids on the Radiation Intensity of the Alkali Metals

The test element and its concentration in solution		λ in mμ	Material added and its concentration, in M	Value of the photocurrent on adding other material, as % of photocurrent of solution without addition of other material			
				Acetylene flame		Illuminating gas flame	
γ/ml	M			together	separately	together	separately
K,50	$1{,}3 \cdot 10^{-3}$	766—769	H_2SO_4, 0,5	84	100	—	—
Na,23	10^{-3}	589—589,6	H_2SO_4, 0,5	96	96	90	96
Na,23	10^{-3}	589—589,6	H_2SO_4, 2,0	73	93	65	92
Na,50	$2{,}2 \cdot 10^{-3}$	589—589,6	H_2SO_4, 1,0	75	93	—	—
K,50	$1{,}3 \cdot 10^{-3}$	766—769	H_3PO_4, 2,0	39	53	—	—
K,39	$1 \cdot 10^{-3}$	766—769	H_3PO_4, 0,1	82	87	68	68
K,39	$1 \cdot 10^{-3}$	766—769	H_3PO_4, 1,0	48	57	24	30,6
Na,23	$1 \cdot 10^{-3}$	589—589,6	H_3PO_4, 0,1	90	95	98	98
Na,23	$1 \cdot 10^{-3}$	589—589,6	H_3PO_4, 1,0	66	82	57	71

TABLE 4

Effect of Phosphates on the Radiation Intensity of Calcium

Ca concentration		λ in mμ	Concentration of $(NH_4)_2HPO_4$, in M	Value of photocurrent on addition of other material, as % of photocurrent of original solution			
				Acetylene flame		Illuminating gas flame	
γ/ml	M			taken together	taken separately	taken together	taken separately
100	$2{,}5 \cdot 10^{-3}$	622	$1{,}65 \cdot 10^{-3}$	65	100	—	—
100	$2{,}5 \cdot 10^{-3}$	422,7	$1{,}65 \cdot 10^{-3}$	65	100	—	—
100	$2{,}5 \cdot 10^{-3}$	622	$1{,}65 \cdot 10^{-3}$	—	—	13	98
40	$1 \cdot 10^{-3}$	422,7	$0{,}66 \cdot 10^{-3}$	73	99	—	—
40	$1, 10^{-3}$	622	$0{,}66 \cdot 10^{-3}$	—	—	14,2	97
20	$5, 10^{-4}$	422,7	$3{,}3 \cdot 10^{-4}$	85,5	100	—	—
20	$5, 10^{-4}$	622	$3{,}3 \cdot 10^{-4}$	—	—	16	95

tain limit, there is a drop in the intensity of calcium radiation; beyond this limit phosphoric acid does not exhibit a quenching effect [17]. Quantitative results testify to the formation of compounds between phosphorus and calcium with ratios of Ca:P = 1:1, 3:2 [18, 19] or even 2:1 [20].

Formation of Compounds between Metal Oxides. A detailed study has been made of the quenching of the radiation of alkaline earth metals in the presence of aluminum salts [17]. At a sufficiently high concentration of aluminum salts, the radiation of the alkaline earth metals can be suppressed completely; this opens up new possibilities for the determination of traces of alkali metals in the presence of the alkaline earths [21, 22]. One suggestion advanced to explain the quenching effect of aluminum on calcium radiation is the formation of stable, sparingly volatile compounds with low thermal conductivity [22], for example $CaAl_2O_4$ [23], which does not succeed in evaporating during its passage through the flame [24].

A Study of the Mechanism of the Effect of Foreign Materials on the Radiation Intensity of the Elements in a Flame. The mechanism of the effect of a material on the radiation intensity of elements in a flame may differ in different cases. For further discussion it is useful to consider the processes which occur on introducing a solution of the salt of an element MeX into a flame (Fig. 1).

The test solution (I) after passing out of the sprayer forms an aerosol consisting of fine drops of solution (II), which, initially, as the result of evaporation of water in the flame, is converted into an aerosol consisting of solid particles of salt (III). When the salt evaporates, a gas MeX (IV) is formed, this being in equilibrium with the dissociation products, atoms of Me and X (V). The atomic gas ionizes partially to give, initially, Me^+ ions (VI), which partially form new compounds with molecules and radicals, for example MeOH (VII). The radiation of the resonance lines is determined by the partial pressure of the metal atoms, while every change in the preceding processes (I – IV) or in those processes occurring in parallel (ionization, formation of hydroxides) will affect the radiation intensity.

A foreign material, contained in the test solution, may depress the radiation intensity of the metal as a result of its action on one of the processes shown in the schematic diagram, since they are all responsible for the partial pressure of the atomic gas or that of the ions and the hydroxide molecules. Which of these processes is affected can be established by using various techniques, for example by measuring the ionization of the flame it can be established whether this process is affected, or, by measuring separately the intensity of the radiation of the atoms, molecules, and ions, it can be established whether changes occur in the formation of new compounds or ions. In the present article, we shall deal with results obtained on introducing the foreign material and a solution of a salt of the test element into the flame separately.

Such a technique permits one to establish whether it is the processes which the atomic gas undergoes, or the preceding processes (spraying, evaporation, and dissociation) which break down.

Technique and Experimental Results. In order to introduce the foreign material separately into the flame, a burner was constructed which was fed from two sprayers (Fig. 2); the spraying efficiency of these sprayers was the same. The burner was fitted in front of the inlet slit of a type UM-2 spectroscope-monochromator; the width of the monochromator slit was 0.1 mm. The light from the outlet slit of the monochromator was focussed by means of a UF-153 lens onto the cathode of a FEU-19 or FEU-22 photomultiplier, for carrying out measurements in the visible and infrared parts of the spectrum respectively. The photomultiplier was fed from a stabilized high-voltage rectifier, permitting smooth changes in voltage up to 2000 volts. A mirror galvanometer with a sensitivity of 5×10^{-9} a/mm of the scale was connected into the anode circuit of the FEU through a voltage divider – sensitivity regulator. The pressure of the compressed air, supplied by a compressor, was measured by a metal manometer, while the pressure of the acetylene was regulated by a reducer, followed by a screw-clip for accurate adjustment; the pressure was finally measured by means of a water manometer. Illuminating gas was taken from the city supply.

In order to study the mechanism of the action of a material on the radiation intensity of any element, solutions of definite concentrations were prepared; they included: solutions of a salt of the test element, and of the foreign element taken separately, and solutions of salts of the test element and foreign element taken together. These solutions were fed into the flame through two sprayers in the following order: the solution of a salt of the test element (left sprayer) – water (right sprayer); the solution of a salt of the test element (left sprayer) – the solution of a salt of the foreign element (right sprayer); the solution of the salts of the test element and foreign element (left sprayer) – water (right sprayer).

TABLE 5

Effect of Aluminum Salts on the Radiation Intensity of Calcium and Strontium

Taken		λ in mμ	Concentration of $Al(NO_3)_3$, in M	Value of the photocurrent of the solution obtained on addition of aluminum nitrate as a % of the photocurrent of the original solution			
γ/ml	mole/liter			Acetylene flame		Illuminating gas flame	
				taken together	taken separately	taken together	taken separately
Ca, 40	10^{-3}	422.7	$2 \cdot 10^{-3}$	30	99	—	—
Ca, 40	10^{-3}	622	$2 \cdot 10^{-3}$	30	99.5	23	100
Ca, 100	$2.5 \cdot 10^{-3}$	422	$5 \cdot 10^{-3}$	31	100	—	—
Ca, 100	$2.5 \cdot 10^{-3}$	622	$5 \cdot 10^{-3}$	30	100	38	98
Sr, 88	10^{-3}	460.8	$2 \cdot 10^{-3}$	35	100	10	98
Sr, 88	10^{-3}	680	$2 \cdot 10^{-3}$	36	100	15	100
Sr, 220	$2.5 \cdot 10^{-3}$	460.8	$5 \cdot 10^{-3}$	31	100	18	97
Sr, 220	$2.5 \cdot 10^{-3}$	680	$5 \cdot 10^{-3}$	31	100	14	95

When the monochromator is adjusted to isolate the lines or the bands of the test element, the readings obtained for the photocurrent in the second case (test element and foreign element taken separately), and in the third case (test element and foreign element taken together) are expressed as percentages of the readings obtained in the first case for the solution of test element alone.

Table 1 contains results obtained with the two sprayers on using readily ionizable metals — cesium and potassium. These experiments were carried out at low concentrations of the test element, at which the effect of ionization is most strongly expressed; only an acetylene flame was used, since it is in this flame that the effect is most pronounced.

The increase in the intensity of the radiation of cesium and potassium differs for differing concentrations of cesium and of the alkali metal added; the intensity decreases with increasing concentration of the main metal and increases with increasing concentration of the element which quenches the ionization. Of essential importance, however, is the fact that the increase in the radiation is almost or exactly the same whether the foreign element is added in solution or from outside; this confirms the assumption regarding the interaction of the alkali metals in the gaseous state.

Table 2 contains the results of experiments on the study of the nature of the "anion effect" in the case of hydrochloric acid and ammonium chloride. The concentration of these materials taken is relatively high in view of their weak effect on the radiation intensity of the elements. Experiments were carried out with acetylene and illuminating gas flames respectively.

Both hydrochloric acid and ammonium chloride act, presumably, by preventing evaporation of the metal, and, in addition, by reacting in the flame gases with the metal. The existence of such a combined effect is testified to by the drop in the radiation intensity which occurs on introducing the other material into the flame both in the same solution as the test element, or through the other sprayer; the drop is, however, greater in the first case.

The effect of sulfuric and phosphoric acids on the radiation intensity of the alkali metals is observed in the results given in Table 3.

Sulfuric acid, in the main, prevents evaporation from aerosol particles, since it has almost no effect on the radiation of potassium and sodium on introducing it separately; phosphoric acid; obviously exhibits the combined effect, since it forms compounds with the alkali metals in the flame, and also prevents evaporation or spraying the latter is especially marked for high concentrations of phosphoric acid.

Table 4 contains results of experiments carried out to establish the way in which phosphate affects the intensity of calcium radiation. The phosphate concentration was two thirds of the calcium concentration in each case.

When phosphate solution was introduced separately into the flame it had absolutely no effect on the radiation intensity of calcium; when, however, the phosphate was the same solution as the calcium it did depress the calcium radiation intensity. Since at low phosphate concentrations, a break down of the spraying processes could not occur,the surface tension and the specific gravity of such solutions hardly differ at all from the corresponding values for pure water), then, obviously, evaporation of calcium from the aerosol particles is inhibited by the solid salt.

Assuming that compounds are formed between phosphorus and calcium in the flame, it can be postulated that these compounds are formed at the moment of evaporation of the solvent from the drop of solution, and are characterized by low volatility.

Finally, Table 5 contains the results obtained during experiments carried out to explain the nature of the influence of aluminum salts on the radiation of calcium and strontium.

In this case again, as can be seen from Table 5, the effect of the aluminum salt is only manifested when the aluminum salt is present in the same solution as the alkaline earth metal salts; thus, aluminum, mainly, prevents evaporation of calcium and strontium from solid aerosol particles, while the mechanism of its action reduces to the formation of compounds with the alkaline earth metals at the moment of evaporation of drops of the aerosol in the flame.

Thus, by adopting the technique of separate introduction of materials into the flame, by using two sprayers supplying one burner, it is possible to obtain experimental confirmation of the mechanism suggested for the effect of foreign materials on the radiation intensity of elements in a flame.

SUMMARY

Using a setup with two sprayers feeding one flame,a study has been made of the mechanism of the influence of a series of materials on the radiation intensity of the alkali and alkaline earth elements in a flame. It has been confirmed that the mechanism of this influence differs in various cases.

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 3. THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF COPPER*

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Many photometric methods are known at present for the determination of copper. The most widely used methods have been described in textbooks and reviews [1 – 2]. For the determination of traces of copper the reagents most widely used are dithizone [3 – 8], and sodium diethyldithiocarbamate [9 – 11]. The drawback of both these reagents is the impossibility of using them for the determination of copper in the presence of bismuth. In the case of diethyldithiocarbamate, manganese, nickel, cobalt, and large amounts of iron also interfere with copper determination. Many other organic reagents and the photometric methods which have been developed on their basis for the determination of copper, have not, hitherto, found wide application, either because they have not been examined sufficiently, or because the reagents are not readily available.

Peive and Ivanova [12] have used thiooxine (8-mercaptoquinoline) – which we have suggested – for the rapid, direct photometric determination of copper in soils without preliminary removal of iron and manganese. In the present article the effect of other elements on the accuracy of copper determination is considered, together with the limits of applicability of the method.

Thiooxine in neutral, acid, and alkaline solutions, forms with cupric ions a dark-brown salt $Cu(C_9H_6NS)_2 \cdot {}^1/_2H_2O$ which is insoluble in water.

Found %: Cu – 15.81; S – 15.97; N – 6.90; H_{active} – 0.28

Calculated %: Cu – 16.18; S – 16.29; N – 7.12; H_{active} – 0.25

The amount of water of crystallization in cupric thiooxinate was determined by the method for the determination of active hydrogen of Chugaev – Zerevitinov [13], rather than by drying (because of the possible danger of oxidizing the complex). The copper complex was dried for analysis in a vacuum at 14 deg. It is possible that some of the water of crystallization may be lost under these conditions, and that in actual fact cupric thiooxinate contains a whole molecule of water of crystallization and not half a molecule.

Cupric thiooxinate is readily extracted by chlorobenzene, bromobenzene, chloroform, amyl acetate, isopropanol; it is not extracted so readily by benzene, toluene, xylene, dichloroethane; and is only very poorly extracted by carbon tetrachloride, carbon disulfide, and is completely insoluble in aliphatic hydrocarbons.

Cupric thiooxinate is completely extracted from both alkaline and acid solutions (Fig. 1).

In order to take its absorption spectrum, cupric thiooxinate was prepared by adding a solution of Cu^{2+} (1:1000) to excess of an acid (pH 1) solution of thiooxine. The brown precipitate which separated out was filtered off, and washed with water, alcohol, and ether, and finally dried. An aliquot of the complex was dissolved in chloroform and its spectrum registered on a SF-4 spectrophotometer. As shown in Fig. 2, the absorption spectrum of cupric thiooxinate has three maxima: the first lies at 252.5 mμ, the second at 275 mμ, and the third in the visible spectrum at 431 mμ. The corresponding molar extinction coefficients are: at $\lambda_1 = 252.5$ mμ, $\epsilon_1 = 31000$; $\lambda_2 = 275$ mμ, $\epsilon_2 = 29000$; $\lambda_3 = 431$ mμ, $\epsilon = 7530$.

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* Communication 2, see J. Anal. Chem. 13, 507 (1958).

Conformity to Beer's law was studied in the usual way by extracting cupric thiooxinate from 2.5 N HCl at a thiooxine concentration of 0.25 g in 50 ml of solution. As the curve in Fig. 3 shows, the calibration curve is linear up to 8 γ of copper in 1 ml of chloroform.

Thiooxine, like all organic reagents of the type R − SH, according to current theoretical ideas, should interact in aqueous solutions only with those elements which form sulfides which are stable towards water. In this connection, even very high concentrations of the alkali, and alkaline earth metals, and also Al, Tl, Zr, Th, Hf, Cr, etc. do not interfere with the determination of copper. In addition to copper, Pd, Ru, Os, Pt, Ag, Au, Hg, Mo, and W also react with thiooxine in strongly acid solutions. The first three elements should therefore be absent; platinum can be tolerated up to about 50 γ. Silver, mercury, and gold form thiooxinates which are not extracted by organic solvents. Silver (even in amounts of 50 γ) interferes with copper determination, presumably as a result of coprecipitation of copper with the very stable silver thiooxinate. The thiooxinates of divalent mercury and trivalent gold do not coprecipitate cupric thiooxinate, and moderate amounts of Hg^{2+} and Au^{3+} (4 and 10 mg respectively) do not interfere with copper determination.

Molybdenum forms a complex, $MoO_2(C_9H_6NS)_2H_2O$, with thiooxine, and, in acid solutions, the stability of this complex is similar to that of cupric thiooxinate. Molybdenum present in amounts of 5 − 10 γ in the test solution can be masked by 0.5 − 1 g of ammonium thiocyanate. Tungsten thiooxinate is insoluble in chloroform and does not interfere with the determination of copper.

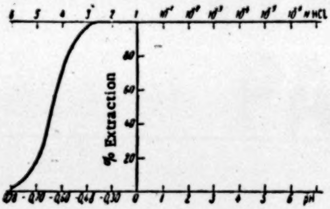

Fig. 1. Extractability of cupric thiooxinate as a function of the reaction of the medium.

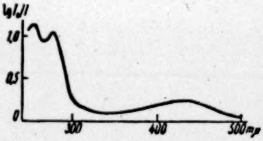

Fig. 2. Absorption spectrum of a 0.000036 M solution of cupric thiooxinate in chloroform.

Very large amounts of tungsten can be kept in solution by means of oxalic acid.

Antimony in amounts greater than 50 γ leads to high results for copper (40 γ).

What is essential is that considerably preponderant amounts of bismuth (which interferes with copper determination by means of the dithizone and diethyldithiocarbamate methods) do not interfere with copper determination by means of thiooxinate.

The effect of other elements on the accuracy of copper determination is shown in the Table.

Both in 2.5 N HCl media, and in weakly acid and alkaline solutions, high concentrations of the common anions (chloride, bromide, fluoride, sulfate, tartrate, oxalate, etc.) do not affect the accuracy of copper determination. In alkaline media, cyanide, when present in an appreciable excess, interferes with complete extraction of copper.

Analytical Procedure. To 15 − 20 ml of a weakly acid (pH 3 − 5) test solution contained in a separating funnel is added 5 ml of a 10% solution of ascorbic acid, followed by 10 ml of a 20% solution of potassium hypophosphite (acidified with hydrochloric acid to the methyl orange end point), 10 ml of a saturated solution of oxalic acid, and 10 ml of concentrated hydrochloric acid (sp. gr. 1.18). The contents of the funnel are shaken, and

TABLE

Determination of Copper in the Presence of Foreign Elements (30 γ Cu taken)

Foreign element (Me), in mg	Ratio Cu : Me	Cu found, in γ	Foreign element (Me), in mg	Ratio Cu : Me	Cu found, in γ
Fe^{II} — 40	1 : 2000	32	Sn^{II} — 10	1 : 500	28
Zn — 10	1 : 500	30	Mn^{II} — 28	1 : 1400	31
Cd — 100	1 : 5000	31	Pb — 10	1 : 500	31
Co^{II} — 5	1 : 250	29	Tl^{I} — 100	1 : 5000	30
Ni — 8	1 : 400	29	As^{V} — 200	1 : 10000	30
W^{VI} — 50	1 : 2500	30	As^{III} — 10	1 : 500	32
Bi^{III} — 6	1 : 300	28	Ge — 50	1 : 2500	31
Sb^{III} — 0,05	1 : 2,5	29	Hg^{II} — 4	1 : 200	28
V^{IV} — 80	1 : 4000	31	U^{VI} — 50	1 : 250	32
Se^{IV} — 10	1 : 500				

then dropwise, with shaking, is added 5 ml of reagent solution (5 g of the potassium salt of thiooxinate is dissolved in 77 ml of water and 23 ml of concentrated hydrochloric acid added; a transparent yellow-orange solution is thereby obtained which is stable in a closed vessel for several weeks). After 2 – 3 minutes, 10 ml of toluene or xylene is added and the contents shaken vigorously for 3 – 4 minutes to extract the cupric thiooxinate. The extract is removed and filtered through a plug of cotton wool; photometric measurements are made on the filrate at 431 mμ, or by means of a S - 42, or S – 47 filter; the copper content is then determined from a calibration curve constructed by means of pure solutions of copper using all the reagents listed above.

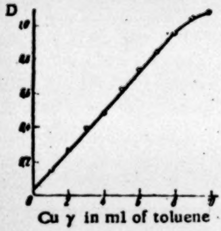

Fig. 3. Conformity to Beer's law of a solution of thioxinate in toluene (filter S-47).

SUMMARY

1. The interaction of thiooxine (8-mercaptoquinoline) with copper in various media, in the presence of foreign cations, has been studied.

2. Cupric thiooxinate $Cu(C_9H_6NS)\cdot {}^{1}/_{2}H_2O$ is stable in strongly acid solutions and is readily extracted by many organic solvents to give solutions with an intense brown color.

3. A photometric method has been developed for the determination of traces of copper (3 – 30 γ) in the presence of predominating amounts of bismuth, manganese, iron, nickel, and other elements.

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DIALKYL- AND DIARYLDITHIOPHOSPHORIC ACIDS AS ANALYTICAL REAGENTS

COMMUNICATION 7. AMPEROMETRIC AND VISUAL TITRATION OF LEAD BY MEANS OF NICKEL DIETHYLDITHIOPHOSPHATE, IN THE PRESENCE OF BARIUM, CALCIUM, ZINC, AND OTHER ELEMENTS*

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Ions of a number of heavy metals, under certain conditions, are almost quantitatively precipitated as compounds with a constant composition by means of solutions of dialkyl- and diaryldithiophosphoric acids. The precipitates separate out, even from very dilute solutions, at a fairly rapid rate. This fact permits one to develop, on the basis of the precipitation reaction, amperometric, visual, and other titrimetric methods of determining certain elements.

Anions of dialkyl- and diaryldithiophosphoric acids are not reduced on the dropping mercury cathode or on the rotating platinum microcathode. Accordingly, amperometric titration based on the cathode current can only be realized for those ions which are reduced on the electrodes indicated.

Recently [1] it was established that anions of diaryldithiophosphoric acids are oxidized on a dropping mercury anode and on a rotating platinum microanode; a linear relation exists between the current and concentration of dialkyldithiophosphate (below 1 millimole/liter) in the case of oxidation on a dropping mercury anode. During electrolysis of a 10^{-3}M solution of sodium diethyldithiophosphate in 0.100 M perchloric acid, the half-wave potential is equal to -0.062 volt with respect to the saturated calomel electrode. Under these conditions, the following reactions occur on the dropping mercury electrode:

$$2Hg \rightarrow Hg_2^{2+} + 2e;$$

$$Hg_2^{2+} + {}^{-}SP(S)(OR)_2 \rightarrow Hg + Hg[SP(S)OR)_2]_2.$$

Thus, the mercury electrode does not behave as an inert electrode. The half-wave potential during oxidation of dialkyldithiophosphates on a dropping mercury electrode becomes more negative with increasing molecular weight of the radical, presumably as a result of a decrease in the solubility of the corresponding mercury dialkyldithiophosphates. The following reaction takes place on a platinum microanode:

$$2{}^{-}SP(S)(OR)_2 \rightarrow (RO)_2P(S)SS(S)P(OR)_2 + 2e.$$

The half-wave potential during electrolysis of a 10^{-3}M solution of sodium diethyldithiophosphate in 0.100 M perchloric acid on a rotating platinum microanode, is equal to +0.696 volt with respect to the saturated calomel electrode.

As an example of the use of a dialkyldithiophosphate for amperometric titration, a description is given in

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[*] For Communication 6, see Bull. Moscow State University, 2, 1958, p. 177.

the present article of the amperometric titration of lead ions by means of nickel diethyldithiophosphate, using a rotating platinum microanode at a potential of +0.8 volt with respect to the saturated calomel electrode. In addition, it is also shown that, under certain conditions, lead can be titrated visually.

It has been pointed out before [2] that lead ions can be quantitatively precipitated by diethyldithiophosphoric acid from neutral and weakly acid solutions.* Under similar conditions the following ions are also precipitated: Hg^{2+}, Ag^{+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Pd^{2+}, Pt^{II}, Ir^{III}, Rh^{III}, Sn^{II}, Sb^{III}, As^{III} (3 N HCl); while the following ions are not precipitated: K^{+}, Na^{+}, NH_4^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+}, Al^{3+}, Zn^{2+}, Ge^{IV}, Cr^{III}, Mn^{2+}, Fe^{2+}, Ga^{3+}, Th^{4+}, V^{V}, U^{VI}. By using complexing agents and regulating the pH, the selectivity of diethyldithiophosphoric acid as a precipitant for lead can be increased.

Lead diethyldithiophosphate is a white, fine-crystalline material with a melting point of 74 deg; it is insoluble in dilute nitric acid, but is soluble in solutions of alkalis, ammonium acetate, and in a number of organic solvents. The sensitivity of detection of lead in weakly acid solutions is expressed by a limit of identification of 2 γ of Pb and a limiting dilution of 1:500,000.

According to published results [4 – 6], the composition of lead diethyldithiophosphate corresponds to the formula $[(C_2H_5O)_2PSS]_2Pb$. The results of our amperometric titration confirmed this formula. The latter was also confirmed by visual titration of a solution of lead nitrate with nickel diethyldithiophosphate to cessation of turbidity, and also by an iodometric method.

An approximate value for the solubility of lead diethyldithiophosphate was determined as follows. A freshly prepared and carefully washed precipitate of lead diethyldithiophosphate was periodically shaken with water for 24 hours at 22 – 24 deg. A known volume (20 – 60 ml) of the saturated solution which had been filtered through a fine filter paper was then transferred to a separating funnel, and excess bismuth nitrate (T_{Bi} = 0.001) added; the bismuth diethyldithiophosphate formed according to the reaction

$$2Bi\,(NO_3)_3 + 3[(C_2H_5O)_2\,PSS]_2\,Pb = 2\,[(C_2H_5O)_2PSS]_3\,Bi + 3Pb\,(NO_3)_2$$

was then extracted with 10 ml of carbon tetrachloride. The extraction was repeated. The yellowish extract was filtered into a 25 ml standard flask and the volume of the solution made up to the mark with carbon tetrachloride; the color of this solution was then measured photometrically on a SF-4 spectrophotometer at 400 mμ (one of the absorption maxima of bismuth) in a 10.01 mm cell, using carbon tetrachloride as the reference liquid. The amount of bismuth diethyldithiophosphate was determined from a calibration curve constructed beforehand using standard bismuth nitrate solution; the solubility of the lead diethyldithiophosphate was then calculated.

The solubility of lead diethyldithiophosphate in water proved to be 1.3×10^{-4} mole/liter (mean of three results near to each other).

The solubility product

$$L_p[(C_2H_5O)_2PSS]_2Pb = 8.6 \cdot 10^{-12}.$$

Qualitative tests showed that lead diethyldithiophosphate is less soluble than lead sulfate but more soluble than lead chromate.**

All that has been said above gives a basis for assuming that precipitation of lead as its diethyldithiophosphate should be suitable for developing an amperometric method for its determination. Certain properties of the lead diethyldithiophosphate formed also permit development of a visual method of titrating lead. Of the greatest practical interest is the possibility of carrying out amperometric and visual titration of lead in the presence of elements such as barium and calcium which are so difficult to separate from lead. These elements often occur together in a number of polymetallic ores, lead-calcium babbites, and lead-barium glass. Existing methods for the separation of lead from barium, strontium, and calcium [8] do not always give reliable results, and are characterized by the long time they take to carry out, and by the complexity of the procedures involved; in addition, they are not suitable for production control. During precipitation of lead by means of hydrogen sulfide from a dilute hydrochloric acid solution containing the alkaline earth metals, it is necessary to create conditions which exclude the formation of sulfuric acid anions (absence of strong oxidizing agents). Separation of

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* Carius [3] was mistaken in his opinion that lead forms a water-soluble salt with diethyldithiophosphoric acid.

** Data on the solubility of lead sulfate and lead chromate can be found in the "Chemist's Notebook" [7].

TABLE 1

Amperometric Titration of Lead by Means of a Solution of Nickel Diethyldithiocarbamate

Lead taken		Metal added in the form of nitrate	Ratio Me/ /Pb	Amount of nickel diethyldithiophosphate sol. used, ml $N_{R_2Ni} = 0.02802$	Lead found	Error	
In ml	In g					In g	In %
0,5	0,00518	—	—	1,80	0,00522	+0,00004	+0,8
1	0,01036	—	—	3,50	0,01028	+0,00008	−0,8
3	0,03108	—	—	10,70	0,03103	−0,00005	−0,2
0,5	0,00518	0,12 K	25	1,75	0,00513	−0,00005	−1
1	0,01036	0,06 NH_4	6	3,50	0,01028	−0,00008	−0,8
1,5	0,01554	0,06 Co	4	5,30	0,01537	−0,00017	−1,1
1	0,01036	0,1 Ni	10	3,55	0,01030	−0,00006	−0,6
0,5	0,00518	0,15 Na	30	1,80	0,00522	−0,00004	−0,8
0,5	0,00518	0,027Cr	5	1,80	0,00522	−0,00004	−0,8
2	0,02072	0,038Mn	2	7,10	0,02061	−0,00011	−0,5
0,5	0,00518	0,065Mg	13	1,80	0,00522	−0,00004	−0,8
0,5	0,00518	0,015Al	3	1,80	0,00522	−0,00004	−0,8
1	0,01036	0,055Zn	5	3,50	0,01028	−0,00008	−0,8
0,5	0,00518	0,21 Sr	40	1,80	0,00522	−0,00004	−0,8
0,5	0,00518	0,25 Ba	50	1,80	0,00522	−0,00004	−0,8
0,5	0,00518	0,12 Ca	25	1,80	0,00522	−0,00004	−0,8

lead from barium, strontium, and calcium by treating their sulfates with ammonium acetate is not quantitative. When lead sulfate is dissolved in ammonium acetate in the presence of calcium and strontium sulfates, strontium sulfate partially dissolves, to the same extent as in the absence of lead sulfate [9]. Satisfactory results can be obtained during separation of lead from barium, strontium, calcium, and magnesium by its precipitation in the form of PbOHCl [10], PbOHBr [11], or PbOHI [11] and then weighing as $PbCrO_4$. Methods of separating lead from the alkaline earth elements by means of organic reagents have not been widely used in practice, mainly because these reagents are not readily available. Morachevskii Zvereva and Rabinovich [12] separated lead from barium by passing a solution in 0.5 N HCl through a column of the anion exchange resins PE-9, EDE-10, and EDE-10-P in the perchlorate form; under such conditions, the anionic complex of lead is completely absorbed by the anion exchange resin, while barium passes into the filtrate. Lead is extracted with water. Methods of determining lead in the presence of the alkaline earth elements are few. The most satisfactory results are obtained during deposition of lead on the anode in the form of its dioxide. This method is, however, not used very much in practice. Existing amperometric methods of titration [13, 14] either do not permit determination of lead in the presence of the alkaline earth elements at all, or yield insufficiently accurate results.

TABLE 2

Visual Titration of Lead with Nickel Diethyldithiophosphate Solution for Various Acid Concentrations (volume of lead nitrate solution − 5.0 ml)

Pb taken, in g	Acid added, in ml	Pb found, in g	Error	
			Absolute in mg	Relative, in %
0,0258	—	0,0256	−0,2	−0,8
0,0258	—	0,0257	−0,1	−0,4
0,0417	—	0,0421	+0,3	+1
0,0835	—	0,0828	−0,7	−0,8
0,0258	5HNO_3, 2,5*N*	0,0266	+0,6	+2,3*
0,0258	5HNO_3, 1,5*N*	0,0260	+0,2	+0,8*
0,0258	5HNO_3, 8 *N*	0,0257	−0,1	−0,4
0,0258	10HCl, 0,1*N*	0,0260	+0,2	+0,8

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* In these experiments urea was not added.

Amperometric Titration of Lead with a Solution of Nickel Diethyldithiophosphate.[*] Amperometric titration was carried out on the usual setup with a rotating platinum microanode. The test solution containing 0.005 – 0.03 g of lead, and up to 0.25 g of barium, strontium, calcium, magnesium, zinc, iron and other elements of Group III, was titrated with 0.1 N nickel diethyldithiophosphate in a supporting electrolyte of 0.1 – 1 N HNO_3 at a potential of +0.8 volt for the platinum microanode with respect to the saturated calomel electrode. After the equivalence point has been reached, there is observed an increase in the diffusion current connected with oxidation of the anode by diethyldithiophosphoric acid to the disulfide.

The method gives satisfactory results (Table 1).

Mercury, silver, copper, cadmium and other heavy metals which form sparingly soluble diethyldithiophosphates interfere with determination of lead.

Visual Titration of Lead with a Solution of Nickel Diethyldithiophosphate. Where a setup for amperometric titration with a rotating platinum microelectrode is not available, lead can be determined quite satisfactorily by a visual method. On addition of nickel diethyldithiophosphate to a solution containing lead, a white turbidity develops, which, on shaking rapidly gives a flocculent, fine-crystalline precipitate; the mother liquor thereupon becomes completely transparent. Experiments have shown that it is quite easy to determine the end point on the basis of the cessation of turbidity on addition of one drop of nickel diethyldithiophosphate solution. Titration should be carried out in a wide, squat beaker placed on black paper. This facilitates establishment of the end point. Observations of the titration should be made from above. Near the equivalence point the beaker is shaken until the mother liquor is transparent. When large amounts of precipitate are formed, the beaker should be inclined so that the precipitate gathers in one place. Usually, a white, continuous film forms on the surface of the liquid being titrated; on addition of a drop of the reagent this film breaks up.

TABLE 3

Visual Titration of Lead with Nickel Diethyldithiophosphate in the Presence of Other Elements (initial volume of solution being titrated 15.0 ml)

Pb taken, in g	Salt added, in g	Ratio Me : : Pb	Pb found, in g	Error	
				Absolute, in mg	Relative, in %
0,0258	$2Ca(NO_3)_2 4H_2O$	13	0,0257	−0,1	−0,4
0,0516	$2Ca(NO_3)_2 4H_2O$	6,5	0,0515	−0,1	−0,2
0,0258	$1Sr(NO_3)_2$	15	0,0257	−0,1	−0,4
0,0258	$1Ba(NO_3)_2$	20	0,0257	−0,1	−0,4
0,0258	$1Ba(NO_3)_2$	20	0,0260	+0,2	+0,8
0,0774	$1Ba(NO_3)_2$	7	0,0773	−0,1	−0,1
0,0258	$1Zn(NO_3)_2 \cdot 6H_2O$	10	0,0257	−0,1	−0,4
0,0258	$1KNO_3$	15	0,0257	−0,1	−0,4
0,0258	$1Al(NO_3)_3 \cdot 9H_2O$	5	0,0260	+0,2	+0,8
0,0258	$1Mn(NO_3)_2 \cdot 6H_2O$	8	0,0257	−0,2	−0,4
0,0258	$1Ni(NO_3)_2 \cdot 6H_2O$	8	0,0260	+0,2	+0,8
0,0258	$1Co(NO_3)_2 \cdot 6H_2O$	8	0,0257	−0,1	−0,4
0,0516	$1Cr(NO_3)_3 \cdot 9H_2O$	5	0,0512	−0,4	−0,8
0,0258	$1Fe(NO_3)_3 \cdot 9H_2O$	5	0,0258	0	0
0,0516	$1Fe(NO_3)_3 \cdot 9H_2O$	2,5	0,0515	−0,1	−0,2

For facilitating observation of the formation of a turbidity in the mass of the solution, after addition of each new portion of titrant, the film formed on the surface is touched with the soaped tip of a glass rod; when this is done the film disappears.

The nickel diethyldithiophosphate solution is standardized by titration with an iodine solution or with a solution of lead nitrate obtained by dissolving a known amount of the chemically pure nitrate. In both cases, the same results are obtained.

The initial concentration of lead in the solution being titrated should be within the limits 0.01 – 0.1 mole/ /liter.

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[*] Synthesis of nickel diethyldithiophosphate and preparation of its solutions have been described previously [2].

Changes in the nitric acid concentration over wide limits (0.01 – 4 N HNO_3) have almost no effect on the titration results for lead, as long as urea is added to the solution being titrated (Table 2).

Chloride ions, in small amounts, do not precipitate lead as the chloride, and do not interfere with the determination.

The visual method gives satisfactory results for the determination of lead in the presence of barium and other elements (Table 3), but takes a rather longer time than most titrimetric methods, and also requires some skill, and is applicable for the determination of relatively large amounts of lead.

The visual method of titrating lead is characterized by its simplicity, and is, probably, of equal value to the complexonometric method of determining lead in the presence of zinc [15].

Amperometric and visual titration of lead in the presence of the alkaline earth and other elements by means of nickel diethyldithiophosphate could be used for developing methods for the analysis of a number of polymetallic ores, lead-calcium babbites, and other materials.

SUMMARY

An amperometric method using a rotating platinum microanode at a potential of +0.8 volt, as well as a visual method of titrating lead with nickel diethyldithiophosphate solution have been developed for determining lead in the presence of the alkaline earth and many other elements. The methods give accurate results.

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SPECTROGRAPHIC QUANTITATIVE DETERMINATION OF HAFNIUM IN ZIRCONIUM DIOXIDE

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Hafnium was discovered more than 30 years ago, but it is only in the last ten years that a number of important applications for this element have been found in modern industry. Very recently the demand arose for very pure zirconium [1]. In this connection, interest in both these elements increased sharply, and it became clear that in the overwhelming majority of cases these elements should be separated from each other as completely as possible.

The close similarity in the physical and chemical properties of hafnium and zirconium complicates the control of the degree of separation of these elements. Accordingly, development of simple and rapid analytical methods for mixtures of the oxides of Hf and Zr is very necessary. Spectrographic analysis is about the only method that would permit rapid and fairly accurate determination of the hafnium concentration of zirconium. The spectroscopist comes up against two characteristic properties in such an analysis. The zirconium spectrum consists of a very large number of lines, while in the hafnium spectrum, in the region available for analysis (2200 – 6000 A), there are no sensitive lines. Accordingly, even determination of as much as some thousandths of a percent of hafnium is by no means easy.

During the last ten years, several articles have been published on the spectrographic determination of hafnium in zirconium [2 – 7]. Only in one of these papers [2] is a method described for determination of thousandths of a percent of Hf. The remaining articles are devoted to samples in which the smallest amounts of hafnium come to hundredths or tenths of a percent.

Gusiatskaia and Rusanov [3] have published a very thorough study of the development of a technique for determination of Hf in Zr within the limits 0.1 to 65% during evaporation of the material from the canal of a carbon electrode in a d.c. arc. By means of additional results the lower limit of determination of hafnium can be lowered to some hundredths of a percent. This article contains a description of an original technique for exciting the Hf tablets from tablets obtained from mixtures of the sample with silver. The technique only requires economical expenditure of sample and permits determination of Hf within the limits 0.5 to 80%. According to the work of Kriuger and others [4] it is possible to determine Hf in amounts from 0.01% on evaporating the material from a carbon electrode.

The work of Kingsbury is very interesting [5].

For determing Hf within the concentration limits 0.01 to 55%, the test material is placed as a thin layer on the flat end of a graphite electrode and fixed there by means of a bakelite solution. The spectrum is excited in the discharge of a low-voltage spark. The standard error characterizing the experimental error is equal to 6%.

The present article contains a description of our work on the determination of hafnium oxide in zirconium oxide in the range of thousandths of a percent to several percent. In order to solve this problem two separate techniques have been developed which differ from those published earlier.

Determination of Low Concentrations of Hafnium Oxide. According to the results given in [2], a mixture of the test material with graphite and barium fluoride is burnt in the canal of a graphite electrode using a 30 amp. d.c. current. The spectra are registered on a spectrograph with a diffraction grating, and the Hf line at

2820.2 A is obtained at a HfO_2 concentration of 0.003%. Because we did not have an apparatus with a diffraction grating at our disposal, we used the KS-55, a prism spectrograph. As our experiments showed, when the spectra were excited under the conditions described in [2], it was found impossible to detect the hafnium line on the strong background when the amount of hafnium present was of the order of some thousandths of a percent.

In order to reduce the background, discontinuous exposure was used, while a totally different method of introducing the sample into the discharge was employed. 50 mg of the calcined and ground zirconium oxide was mixed in a mortar with 1 ml of glycerol for 4 minutes. A conical crater 1.5 mm deep was made in the lower electrode; the upper electrode was sharpened to a truncated cone. The electrodes were adjusted by shadow projection until the interelectrode gap was 3.5 mm, and, with the slit closed for 10 seconds, the a.c. arc switched on. The holder of the lower electrode was then withdrawn to the side and a drop of the glycerol suspension placed on the graphite by means of a pipet; the holder was then replaced in position. The glycerol evaporated rapidly and the test material in the form of a thin layer of powder was left securely on the electrode surface. Next, the slit was opened for 10 seconds while the arc was switched on, another drop of the suspension was then placed on the electrode. In all, 4 drops of suspension were placed on the electrode during a total exposure time of 40 seconds. The slit was illuminated with a three-lens system; the arc current used was 20 amperes. It was found essential to work at a definite rhythm. It was also found essential not to place the suspension on an electrode which was either too hot or too cold. In both extremes, loss of test material occurred.

The spectra were photographed on "Spectrographic Type II" plates with a sensitivity of 16 GOST units; the slit width was 0.01 mm. The developer used was special contrast developer D-11, the developing time being 6 minutes at 20 deg. The Hf line at 2940.77 I A was observable against the background, when the hafnium concentration was equal to a few thousandths of a percent.

Determination of unknown amounts of hafnium was carried out by means of a calibration curve drawn within the coordinates logarithm I^{Hf}/I^{Zr}, logarithm c, the background being taken into account. The line Zr 2942.3 A was used as the reference line. The spectra of standards were photographed on the same plates as those used for test samples. A typical calibration curve for the determination of HfO_2 in amounts ranging from a few thousandths to some tenths of a percent is shown in the diagram. The slope of the curve is about 0.67.

Appreciable amounts of CO and O_3 are formed in the discharge arc at 20 amperes. The work should therefore be carried out with adequate ventilation. The burning arc should be confined within a case with a door which can be conveniently opened.

Determination of Average Concentrations of Hafnium Oxide. Hafnium, at concentrations ranging from some tenths of a percent to a few percent, was determined on the average spectrographs Q-24 and ISP-22, using three-lens illumination of the slit. One drop of the test suspension in glycerol was placed by means of a pipet on the face of an unheated pointed carbon electrode. The metal stand and electrodes were placed on an electric hot plate, and the glycerol burnt off in the course of 20 minutes until no more fumes were given off. A thin layer of test material was, in this way, left on the electrode surface.

The spectrum was excited in a d.c. arc, the test material being connected to the anode.* The upper electrode was sharpened to give a truncated cone. The arc gap was 3.5 mm, the current was 6 amps., while exposure time was 30 seconds.

Analysis was carried out on the basis of a solid calibration curve using the analytical lines Hf 2641.4" — Zr 2619.2" A. The calibration curve was constructed within the coordinates logarithm I_{Hf}/I_{Zr}, logarithm c, the background being taken into account. The calibration curve is shown in the diagram. The slope was equal to one. The glycerol suspension should be used for analysis on the same day as it is prepared, since, on keeping the suspension for a long time, there occurs a gradual change in the relative intensities of the lines in the spectra.

DISCUSSION OF RESULTS

The techniques used most often for the determination of Hf in Zr are based on evaporation of test samples from the canal of a carbon electrode. In order to ensure more even burning of the test material, it is customary to mix the test sample with powdered graphite. Our earliest experiments on the determination of average amounts

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* Analysis can also be carried out with an a.c. arc.

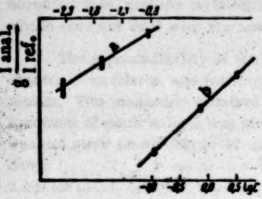

Diagram. Calibration curve for determination of Hf in Zr: a) For determination of low Hf concentrations; b) for determination of average amounts of Hf.

of hafnium by evaporation from a canal, showed that, even in the presence of graphite powder, sputtering of test material from the electrode canal was not a rare occurrence; this leads to weakening of the spectrum and to a sharp change in the relative intensities of the lines. This, in turn, leads to considerable experimental errors.

By placing the test material in the form of a suspension on a flat or almost flat electrode, sharp variations in the absolute intensity of the spectra can be avoided when the electrodes are set up properly and the interelectrode distances are reproduced readily. When this technique is used for introducing the test material into the discharge, even strong variations in the absolute intensity of the spectra do not affect the value of the relative intensities of the lines.

Experiments were carried out in order to clarify the effect of certain factors on the experimental accuracy. Spectra of samples containing approximately 1.3% and 0.8% of hafnium respectively, were photographed. The values of the blackening of the Hf lines were 0.8 – 0.9 and 0.45 – 0.5 respectively. The results are given in the Table. Changing the time for which the powder is triturated with glycerol from 5 to 35 minutes was found to have no effect on ΔS for the analytical pair of lines. A characteristic feature is that changes over wide limits in the amount of sample placed on the carbon had hardly any effect at all on the absolute intensity of the lines and on the values of ΔS. In order to check this, emulsions containing 20, 40, and 60 mg of powder per ml of glycerol were prepared. The time for which the electrodes were dried on the electric hotplate after all the fumes had ceased to come off, was also found to have no effect.

The glycerol suspension gradually soaked into the carbon. A series of tests were therefore carried out to establish the effect of the soaking in of the glycerol into the carbon on the value of ΔS. No appreciable changes in the values of ΔS could be found between spectra obtained from electrodes dried immediately after placing the suspension on them, and spectra obtained from electrodes dried 2.5 hours after placing the suspension on them.

Effect of Various Factors on the Value of ΔS for the Lines Hf 2641.4 and Zr 2619.2 A

Duration of trituration of suspension			Amount of sample on the electrode			Time for which electrode was dried			Duration of soaking of the carbon with glycerol		
Time in min	ΔS	ΔS mean	Amount in mg	ΔS	ΔS mean	Time in min	ΔS	ΔS mean	Time in hours	ΔS	ΔS mean
7	0,04 0,06 0,08	0.06	20	0,29 0,26 0,28 0,25	0,27	6 *	0,22 0,19 0,20 0,22	0,21	Immediately after placing the glycerol on carbon electrode	0,26 0,25 0,29 0,29	0,27
14	0,07 0,05 0,06	0.06	40	0,27 0,31 0,27 0,26	0,28	20	0,24 0,27 0,25 0,26	0,25	2,5	0,29 0,28 0,30 0,31	0,29
21	0.06 0,08 0,06	0,07	60	0,25 0,28 0,26 0,29	0,27	50	0,27 0,25 0,24 0,24	0,25	—	—	—

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* Incomplete burning off of the glycerol.

The fact that none of the factors listed above was found to affect the relative intensity of the lines, gives a favorable basis for carrying out analysis with satisfactory accuracy. This fact also permits analysis of samples containing average amounts of Hf by means of a constant calibration curve, without having to resort to photographing the spectra of standards. We had used glycerol suspensions previously for the determination of boron in boron carbide, and the technique fully justified itself in that case, also. This technique was borrowed from [8], which does not deal with the analysis of mixtures of Hf and Zr.

The reproducibility of the values of the relative intensities of the lines, in replicate photographs of the spectra of standards, and for samples of average concentration (0.2 – 3%) can be characterized by the following results. The maximum absolute deviation of the value of logarithm $I_{anal.}/I_{ref.}$ from their mean value (the spectrum of each sample was photographed 3 times) was equal to 0.03. In 83 cases out of a 100, this deviation was not more than 0.02; in 52 cases it was not more than 0.01. The maximum deviation of the value of logarithm $I_{anal.}/I_{ref.}$ is equal to 0.05. The probable error when three photographs of the spectra were taken was ± 2.1% for mean hafnium concentrations.

For samples with hafnium oxide concentrations equal to 0.005 – 0.007%, the experimental accuracy is lower. In this case the density of the Hf line differs insignificantly from the background and errors made during the photometric measurements start to play an essential role. The probable experimental error for thousandths of a percent of hafnium oxide, is ± 19% when three photographs are taken. The error drops to ± 13% when some hundredths of a percent is to be determined. For the determination of low concentrations, the spectra of three standards are taken on each photographic plate.

One worker can carry out ten analyses in the course of a working day.

SUMMARY

Methods have been developed for the quantitative spectrographic determination of 0.005 to 3% of hafnium in zirconium dioxide on the ISP-22 and KS-55 spectrographs. Samples are burnt as thin layers of powder on carbon electrodes. Experimental accuracy is sufficient for controlling the separation of hafnium from zirconium.

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POTENTIOMETRIC TITRATION OF SILVER, COPPER, LEAD AND THALLIUM BY MEANS OF THIOACETAMIDE

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Thioacetamide CH_3CSNH_2 is used in analytical chemistry as a substitute for hydrogen sulfide for the precipitation of metals in qualitative and quantitative analysis. It is a solid which is fairly stable in neutral aqueous solutions, and, in contrast to hydrogen sulfide, does not possess toxic properties (it does not have an unpleasant odor). When thioacetamide is used as the precipitant, the metal sulfides are precipitated as coarse crystals which are readily filtered, and hardly trap foreign ions at all. By regulating the precipitation conditions, it is possible to alter the rate and sequence of the precipitation of the metal sulfides.

Thioacetamide was used by Ivanov in 1934 [1] for detecting heavy metals in pharmaceutical products. Vavilov [2] has recommended this reagent for the detection of bismuth. Subsequently, this reagent was used as a group reagent in qualitative analysis [3 – 5].*

The possibility of using thioacetamide for the gravimetric determination of heavy metals has been studied in detail by Flaschka and co-workers [6]. The same author has suggested using thioacetamide for the precipitation of metal sulfides in combination with complexons.

At present there is a very large number of examples of the use of thioacetamide for the determination of various metals [6 – 13].

We thought it would be interesting to study the possibility of using this reagent for the potentiometric titration of certain metals by precipitating them as their sulfides.

In the work described here an attempt was made to use thioacetamide as a titrant for the potentiometric titration of silver, copper, lead and thallium.

The main difficulty which arises during the use of thioacetamide as a source of hydrogen sulfide during potentiometric titration is its low rate of hydrolysis in aqueous solutions. According to the work carried out by Swift and Butler [13], the constant of the hydrolysis rate of thioacetamide at 90 deg has a value of 0.21 mole/liter. At higher pH values, and in the presence of lead ions, the constant of the hydrolysis rate increases by more than two orders. Under such conditions, the authors note that, in the presence of lead salts, the order of the reaction changes in comparison with hydrolysis in pure solutions.

The rate of precipitation of the metal sulfides is, in most cases, too low for the use of thioacetamide as a titrant during potentiometric titration.

Only precipitation of silver ions from ammoniacal solutions proceeds with sufficient speed for practical application. Other metal ions, such as copper, mercury, lead, thallium, etc. are precipitated very slowly by thioacetamide. Increasing the temperature and changing the pH of the solutions, although they affect the precipitation rate, in that they increase it, still do not do so to a sufficient extent to make the use of thioacetamide as a titrant for these metals feasible.

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* Apparently, thioacetamide was used as a group reagent in qualitative analysis as long ago as 1928 (see [2]).

On the basis of a series of experiments which we carried out we found that the rate of precipitation of lead and some other metals by this reagent can be increased to a considerable degree by adding small amounts of hydrazine hydrate to the reaction mixture.

While in the case of precipitation of copper sulfide, the increase in the rate of precipitation in the presence of hydrazine hydrate can be ascribed to differences in the rate of precipitation of Cu^{+} as compared with that of Cu^{2+}, i.e. this increase can be explained by the reducing properties of hydrazine hydrate; in the case of the precipitation of the sulfides of lead, thallium, and other metals, such an explanation is no longer possible. The part played by hydrazine hydrate, in these cases, is, presumably, considerably more complicated, and requires special study.

Test element	Taken, in g	Found, in g	Difference in g	Test element	Taken, in g	Found, in g	Difference in g
Silver	0,1082	0,1085	+ 0.0003	**Lead**	0,1848	0,1850	+ 0,0002
	0,1134	0,1131	— 0,0003		0,1495	0,1493	— 0,0002
	0,1214	0,1209	— 0,0005		0,1583	0,1582	— 0,0001
	0,1358	0,1355	— 0,0003				
Copper	0,1026	0,1024	— 0,0002	**Thallium**	0,1968	0,1966	— 0,0002
	0,1148	0'1144	— 0,0004		0,1665	0,1668	+ 0,0003
	0,1206	0,1209	+ 0,0003		0,1327	0,1326	— 0,0001
	00,1336	0,1335	— 0,0001		0,0957	0,0954	— 0,0003
	0,1372	0,1373	+ 0,0001				

By making use of this property of hydrazine hydrate, we have developed techniques for the potentiometric determination of copper, lead and thallium by means of thioacetamide.

Titration was carried out with the aid of a sulfide indicator electrode made from synthetic argentite (Ag_2S); this electrode has been described previously [14]. The reference electrode was a saturated calomel electrode. The e.m.f. was measured on a PPTVI potentiometer. The compensation current was measured on a M91 galvanometer to 10 μa. The solution was agitated with a mechanical stirrer during titration. The thioacetamide solution was prepared by dissolving material which had been recrystallized twice (m.p. 110 deg) from benzene in distilled water. The thioacetamide solution was standardized against an accurately weighed aliquot of a sample of the test metal.

The thioacetamide solution was stored in a flask with a ground-glass stopper. The factor of the thioacetamide solution remained constant over a long period (about 2 months), and the solution did not require any special storage conditions.

Determination of Silver. From ammoniacal solutions, in the presence of sodium or calcium ions, precipitation of silver ions by thioacetamide proceeds instantaneously. The electrode potential is established very rapidly during titration, and titration proceeds without any complications. A typical titration curve obtained during titration of silver with thioacetamide is shown in Fig. 1.

As the results given in Table 1 show, the accuracy obtained during determination of silver by titration with thioacetamide is not less than the accuracy of methods widely used in practice.

Preparation of samples for analysis, and the titration itself are carried out as follows: 0.1 – 0.2 g of silver is dissolved in the minimum amount of nitric acid, the solution is then evaporated almost to dryness for removal of nitrogen oxides. The crystals obtained are dissolved in a small amount of water and the solution transferred to a 100 ml standard flask. 10 ml of this solution, which is taken for titration, is placed in the titration cell and 20 ml of the following mixture added: $0.2\ N\ NH_4OH + 0.2\ N\ NaNO_3 + 0.03\ N\ Ca(NO_3)_2$.

Titration is carried out in the cold with stirring. Calculations are based on the factor of the thioacetamide which has been established by means of a standard sample of silver under the same conditions. The equivalence point is established by constructing a curve within the coordinates $d\varepsilon/dv$, V.

Determination of Copper. Precipitation of copper sulfide by means of thioacetamide from solutions containing divalent copper, proceeds only after long standing – even on heating. Appreciably more rapid is the precipitation of copper sulfide from solutions of univalent copper obtained by reducing the divalent copper with hydrazine hydrate.

In such cases cuprous sulfide is formed immediately, even at room temperature. The potential of the sulfide electrode is established very rapidly during titration. A curve obtained during titration of copper with thioacetamide is shown in Fig. 1. As in the case of silver, the titration curve exhibits a large potential jump near the equivalence point.

Preparation of samples for analysis is carried out in exactly the same way as for silver. For one determination 10 ml of a solution of divalent copper with a content of 0.01 – 0.015 g of Cu is taken, and 30 ml of 1 N sodium acetate and 5 ml of NH_4OH (25%) added, hydrazine hydrate (1:5) is then added until the blue color disappears.

Thioacetamide is added with stirring to the mixture thus obtained. Reduction of the copper must be carried out very carefully, precautions being taken to ensure that the amount of hydrazine hydrate taken is such that a large excess of it does not remain in the solution. When a large excess of this material is present, the electrode potential is established poorly and titration is not quantitative. The reproducibility and accuracy of the results obtained for the determination of copper are fully satisfactory (Table 1). Calculations are based on the factor for thioacetamide established beforehand by means of a standard copper sample.

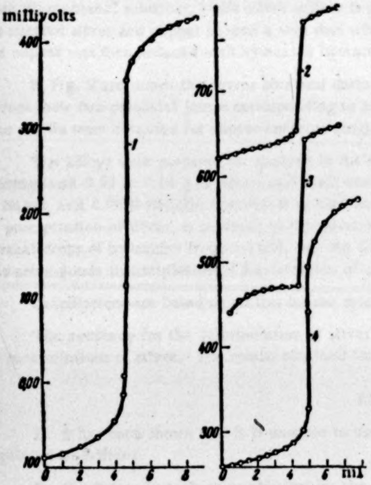

Fig. 1. Titration curves of metals with thioacetamide:
1) Silver; 2) lead; 3) thallium; 4) copper.

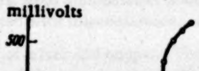

Fig. 2. Titration curves for a mixture of silver and copper ions.

Determination of lead is carried out in the same way as for silver and copper. To 10 ml of a solution containing 0.01 – 0.015 g of Pb is added 10 ml of 10% NaOH and the solution heated to 70 – 80 deg, a few drops of hydrazine hydrate is then added. A curve obtained during titration of lead with thioacetamide is shown in Fig. 1.

As is evident from Table 1, the results obtained for lead proved to be very good.

Determination of Thallium. Flaschka [11] has shown that univalent thallium is not precipitated from neutral and acetic acid solutions by means of thioacetamide; from ammoniacal solutions, thallium sulfide precipitates instantaneously. Nevertheless, the potential of the sulfide electrode is established poorly in ammoniacal solutions. Addition of small amounts of hydrazine hydrate renders the potential of the sulfide electrode more stable. The stability of the potential is also enhanced by heating the solution.

The curve obtained during titration of thallium with thioacetamide has a characteristic shape (Fig. 1). The potential jump at the equivalence point is very sharp; nevertheless, its absolute value is less than that of the other metals studied. The sharp jump on the titration curve can be observed at concentrations down to 2 – 3 γ of Tl in 10 ml of solution.

Metal thallium is dissolved in dilute nitric acid. 10 ml of solution containing 0.01 – 0.02 g of Tl is taken for titration, 25 ml of water is added and the solution warmed 70 – 80 deg; 25 ml of 25% NH_4OH is then added, followed by 2 – 3 drops of hydrazine hydrate (1:2).

The thioacetamide solution was standardized against a standard solution of thallium nitrate. As Table 1 shows, the results obtained for the potentiometric determination of thallium are accurate enough.

For the determination of silver and copper in copper-silver alloys, using one aliquot of test sample, use was made of, on the one hand, differences in the solubility of the sulfides of copper and silver, and, on the other hand, of differences in the precipitation rate of these sulfides.

As mentioned already, direct precipitation of divalent copper by thioacetamide proceeds extremely slowly from ammoniacal solutions, while silver sulfide is precipitated immediately from such solutions. Accordingly, we titrated silver and copper in such a way that silver was precipitated first from ammoniacal solution, while the copper was then reduced with hydrazine hydrate and finally precipitated with thioacetamide.

In Fig. 2 are shown the curves obtained during titration of mixtures of silver and copper. The titration curves show two potential jumps corresponding to successive precipitation of silver and copper. The most accurate results were obtained for copper contents ranging from 10 to 90%.

The alloys were prepared for analysis in the same way as the separate metals. To 10 ml of solution containing from 0.01 to 0.05 g of silver, and itself contained in the titration cell, is added 30 ml of a mixture of 0.2 N $NaNO_3$ and 0.03 N NH_4OH; titration is carried out until the first potential jump, corresponding to completion of precipitation of silver, is reached; to this solution is then added 5 ml of 25% ammonia solution, followed by several drops of hydrazine hydrate (1:5), and the titration continued until the second potential jump is reached; this corresponds to completion of precipitation of copper.

Calculations are based on factors for the thioacetamide established beforehand for each metal separately.

The accuracy for the determination of silver is the same as that obtained during determination of silver in pure solutions of silver. The results obtained for copper are on the high side.

SUMMARY

1. It has been shown that it is possible to use thioacetamide for potentiometric titration of metals precipitated as sulfides.

2. Conditions have been established for the potentiometric titration of silver, copper, lead, and thallium, and also for silver-copper alloys in which thioacetamide is used as the titrant.

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A SIMPLIFIED METHOD FOR INTERNAL ELECTROLYSIS USING A DIAPHRAGM

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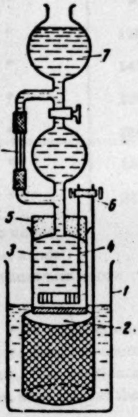
Of the existing methods used in analytical chemistry for internal electrolysis, only those which do not involve diaphragms have received wide practical application [1]. Diaphragm methods of internal electrolysis [2] are used much more rarely in view of the complexity of the apparatus and the duration of the electrolysis process which is determined by the high ohmic resistance of the electrolyzer. The method of internal electrolysis with a protective film [3], although it is simple from the point of view of the design of the apparatus, is nevertheless still inferior to the diaphragmless method from the point of view of the duration of electrolysis, and, at the same time, in contrast to the diaphragm method, it is not applicable for the determination of large amounts of metal.

Were it possible to eliminate the phenomenon of cementation by a simpler method, then, undoubtedly, the internal electrolysis method, in view of its simplicity and convenience, would receive even more wide application in analytical practice.

Bearing in mind the advantages of internal over external electrolysis, we decided to study the possibility of developing a simplified diaphragm method which would permit separation of average and large amounts of metal, fairly rapidly.

In order to speed up the process of metal deposition, we departed from the use of thick diaphragms, and used No. 1 large-pore glass diaphragms, the introduction of which into the electrolyzer does not increase the ohmic resistance of the latter significantly. Penetration of catholyte into the anode space was prevented in the method under test by meeting the catholyte liquid with a weak flow of anolyte; this, needless to say, is necessary only in the initial period of electrolysis, in the course of the 10 – 15 minutes when most of the test material is deposited from solution. After this, possible mixing of the solutions should not present any danger, since, at low concentrations of test material, cementation will not occur.



Schematic diagram of the apparatus used for internal electrolysis using a No. 1 coarse-pore diaphragm.

The apparatus suggested by us for internal electrolysis is shown schematically in Fig. 1. The apparatus consists of a beaker 1, with a capacity of 250 – 300 ml, into which the test solution is poured, a platinum grid cathode 2, a glass beaker 3, 80 mm tall and 40 mm in diameter, with a bottom made from No. 1 coarse-pore glass, and designed for separating the anode space from the cathode space. A beaker of this type is readily made from a normal glass funnel with a No. 1 porous filter disc, by cutting off the conical part of the funnel below the disc, and rounding off the edges after cutting off level with the base of the disc. The top of the beaker is closely sealed with a rubber stopper 5 with two holes drilled through it; through one of these holes is fitted a tube from the supply reservoir containing the anolyte, while through the other hole is fitted the upper part of the anode 4 for connecting it through a brass terminal to the cathode. Connection of the anode with the cathode is made in such a way that the top part of the cathode grid is at the same level as the porous bottom of the beaker 3. The supply reservoir is a dropping funnel of a modified type with a spherical bulb underneath the tap, and two side tubes between which a capillary 7 is fitted by means of rubber tubing. Through this capillary, when the tap of the reservoir is closed, the anolyte passes slowly into the beaker 3, thereby creating the necessary head of anolyte liquid on the diaphragm; thanks to this, penetration of catholyte into the anode space is completely prevented.

The experimental procedure used was as follows. The supply (pressure) reservoir and the diaphragmed beaker containing the anode were filled with anode liquid. This was carried out by opening the tap of the reservoir, and placing a tall beaker containing anolyte heated to 70 – 80 deg under the diaphragmed beaker; the anolyte was then sucked by mouth or by means of a water pump through the upper part of the reservoir. After connecting the anode to it, the apparatus was immersed in the test solution of cupric sulfate heated beforehand to 70 – 80 deg, so that only the lower part of the diaphragmed beaker was in the solution. Completeness of deposition of copper was controlled by a spot test with potassium ferrocyanide or sodium sulfide. The time taken for complete deposition of copper, depending on the amount of copper, varied from 40 to 90 minutes. When electrolysis was complete, the apparatus was rapidly removed from the solution and immersed in distilled water for several minutes; the cathode was then disconnected, washed with water and then with alcohol, dried, and, after cooling, weighed.

TABLE 1

Determination of Copper by the Simplified Method of Internal Electrolysis (anolyte – potassium chloride)

Copper taken, in mg	Copper found, mean of 3 – 4 determinations, in mg	Duration of electrolysis, in minutes	Mean deviation of individual determinations from the mean		Deviation of the mean value found from that taken	
			in mg	in %	in mg	in %
46.85*	46.73	40	0.30	0.63	0.12	0.25
118.8*	118.5	55	0.50	0.43	0.30	0.26
142.8*	142.5	65	0.00	0.00	0.30	0.21
190.8*	190.5	80	0.20	0.10	0.30	0.14
238.5*	238.4	90	0.20	0.08	0.10	0.05
142.8**	141.7	65	0.20	2.10	1.10	0.80
253.0***	252.8	90	0.10	0.06	0.20	0.07

---

* Zinc anode

** Iron anode

*** Aluminum anode

Pure reagents were used in the course of the experiments carried out. The zinc and aluminum anodes were prepared from the chemically pure metals. The solution of cupric sulfate was standardized by external electrolysis. The solution was prepared for analysis in the usual way. Solutions of potassium chloride and potassium nitrate were used as the anolyte.

Tests showed that the suggested method of internal electrolysis permits determination of both average and large amounts of copper.

It should be pointed out that when a zinc, or an iron anode immersed in a saturated solution of potassium chloride was used, dissolution of the anode proceeded slowly and was not accompanied by evolution of appreciable amounts of gas. When, however, an aluminum anode was used, the anode dissolved vigorously and considerable amounts of hydrogen were evolved. In order to prevent expulsion of anolyte from the diaphragmed beaker, and to prevent the cessation of current flow which accompanies this, the apparatus was provided with the spherical vessel under the tap in order to collect the gas.

As is evident from Table 1, the accuracy and reproducibility of the results for copper are fully satisfactory.

Results for the determination of copper with a zinc anode immersed in a saturated solution of potassium chloride, in solutions containing some ferrous sulfate in addition to copper, are given in Table 2. As can be seen from Table 2, the presence in the test solution of iron, even in amounts which are twice that of copper, does not affect the results for copper

TABLE 2

Determination of Copper in the Presence of Divalent Iron

Copper taken, in mg	Iron added, in mg	Copper found, in mg	Mean deviation of the individual determinations from the mean		Deviation of the mean found from that taken	
			In mg	In %	In mg	In %
238,2	224,0	237,6	0,30	0,40	0,60	0,24
238,2	448,0	237,4	0,20	0,20	0,80	0,33

Special tests showed that other salts of the alkali metals can be used instead of potassium chloride as the anolyte.

In conclusion, the applicability of the method we had developed was checked for the determination of copper in alloys. A standard sample of Muntz metal certified as containing 60.40% of copper was taken for analysis. The alloy was dissolved, and the solution obtained prepared for analysis in the usual way. The determination was carried out with the aid of a zinc anode. The mean value for five determinations was 60.39%.

SUMMARY

A simplified apparatus has been designed for internal electrolysis in which a diaphragm made of a No. 1 large-pore glass plate is used. It has been shown that it is possible to determine average and large amounts of copper by means of this apparatus with reasonable accuracy and rapidity.

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THE DETERMINATION OF MICRO AMOUNTS OF COPPER, LEAD, AND ZINC IN NATURAL WATERS AND IN SOIL EXTRACTS

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The coexistence of copper, lead, and zinc is common for natural waters in territories where polymetallic ore deposits are found. An interest in a simple field method of determining the elements is therefore a natural one.

The separation and determination of copper, lead, and zinc by means of dithizone is based on accurate control of the pH of the solutions and the use of cyanide for masking Cu and Zn during determination of lead [1, 2]. The poisonous nature of KCN is the most essential drawback for its use in the field. Moreover, potassium cyanide can lead to low results for lead [1, 3].

Two methods have been developed for the separation and subsequent determination of Cu, Pb, and Zn, in which potassium cyanide is not used.

In the first variant, copper is removed by extraction of the dithizonate in a hydrochloric acid medium (0.1 – 0.5 N), or the total dithizonates of copper, zinc, and lead are extracted in a weakly ammoniacal medium in the presence of ammonium citrate and the lead and zinc then re-extracted with 0.01 – 0.02 N HCl.* In both cases copper is determined on the basis of the mixed color in the organic extract. The aqueous layer is made alkaline with ammonia and the dithizonates of zinc and lead extracted. We have found that at sufficiently low pH values (about 6), an aqueous solution of thiosulfate will readily re-extract lead from the extract without touching the zinc dithizonate. When the separated aqueous re-extract is subsequently made alkaline with ammonia, the lead is again extracted with a solution of dithizone in CCl_4 and the lead is then determined by the monochromatic method [1]. The zinc remaining in the organic layer is evaluated by comparison with standards, or is re-extracted and titrated with dithizone.

The second method is based on differences in the stability of the diethyldithiocarbamates of copper, lead, and zinc dissolved in carbon tetrachloride, with respect to hydrochloric acid. In aqueous acid solutions, diethyldithiocarbamic acid breaks down rapidly [4]. On the other hand, heavy metal carbamates extracted by carbon tetrachloride are much more difficult to break down with acids [5, 6]. A study of the stability of the carbamates of copper, lead, and zinc dissolved in CCl_4 led us to conclude that it should be possible to separate these metals by re-extraction with hydrochloric acid of varying concentrations. Zinc carbamate is completely re-extracted with 0.1 N HCl, which does not, however, affect lead carbamate. Lead carbamate is decomposed by 1.0 N HCl (completely by 3 N HCl). Copper carbamate is not decomposed even on shaking with 6 N HCl. Zinc and lead are determined in the re-extracts by means of dithizone.

a) Separation of Zinc and Lead by Means of Thiosulfate. The analytical procedure followed depends on whether water or an acid extract of solid materials is being analyzed. During the analysis of large volumes of test water, preliminary acidification, which is necessary for the extraction separation of copper, is undesirable, because of the possibility of introducing contamination with the HCl. To 0.5 liter of the test water was added 2 ml of a 25% solution of ascorbic acid or 5 ml of a saturated solution of ammonium citrate purified by means of dithizone, and the pH of the solution adjusted to a pH of 8 — 8.5 with ammonia. Using 5 ml lots of a solution of dithizone in CCl_4 for extracting, the mixture of dithizonates of copper, zinc, and lead was extracted from the solution by vigorous shaking for 3 minutes. Extraction was repeated with fresh lots of dithizone until the dithizone ceased to change color. The combined extracts were then shaken for 2 minutes with two lots of 5 ml of 0.10 — 0.15 N HCl and these re-extracts combined. The CCl_4 layer was washed with 10 ml of "the metal-free" water, which was also combined with the re-extract. The re-extract contained the zinc and lead, while copper remained in the organic layer. Copper dithizonate was broken down by evaporating the CCl_4 and lightly calcining the residue; copper was then determined in hydrochloric acid solution as its dithizonate by the mixed or monochromatic methods [1]. The re-extract containing Zn and Pb was neutralized to phenol red by means of ammonia, and was then titrated with dithizone to a small excess of the latter. The extract was washed with ammonia (1:300) in order to remove excess dithizone, and then washed with the "metal-free" water, after which it was shaken up with 5 ml of 10% $Na_2S_2O_3 \cdot 5H_2O$ solution for 1 minute, the thiosulfate solution had been purified beforehand with dithizone and its pH adjusted to 5.5 — 6.0. The pH of the thiosulfate solution was regulated (on the day the analysis was carried out) by means of 0.01 N HCl, the latter being added dropwise with stirring. Measurements were made with a glass electrode; nevertheless, it was found that it was sufficient, when dealing with the same batch of reagent, simply to prepare a small amount of solution and establish the number of drops of 0.01 N HCl that need to be added to 50 ml of the solution (usually 1 — 3 drops); in this way there is no need to resort to a pH meter but simply use the number of drops of HCl already established. The re-extract was made alkaline with ammonia to the phenol-red endpoint; lead was then determined by extraction titration with a solution of dithizone in CCl_4, the dithizone factor with respect to lead being 2 — 4 γ.

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* Extraction is best carried out in an acid medium when low volumes of test solution are dealt with, while when large volumes (because of the necessity of preparing large amounts of very pure HCl and ammonia) of test solution are being examined extraction is best carried out from a weakly ammoniacal medium.

TABLE 1

Determination of Zinc and Lead

pH of thiosulfate solution	Amount of lead found in the aqueous layer as a percentage of that taken	Zn found in the CCl_4 layer after re-extraction of Pb, as a percentage of the Zn taken
6.5	50	125—100
6.2	60—80	110—100
6.0	80—100	~ 100
5.8	80—100	~ 100
5.6	80—100	~ 100
5.4*	90—110	~ 100
5.3**	> 100	~ 100

*At low ratios of Pb:Zn the results were high for Pb.

**The results for Pb were often high. Rapid decomposition of thiosulfate.

After removal of the lead, zinc was determined directly in the CCl_4 layer (when the color corresponded to that of one of a standard series) or by re-extraction with 0.01 — 0.02 N HCl; in the latter event, after re-extraction, the solution was neutralized with ammonia to the phenol-red endpoint, and the zinc was determined like lead, by extraction titration, the dithizone factor with respect to zinc being 1 — 2 γ Zn.

During the analysis of hydrochloric extracts it was found best to choose the volume of aliquot to be taken on the basis of the "total metals"* content determined beforehand. "Total metals" was determined on a separate aliquot, the solution was neutralized with ammonia to a pH of 8 – 8.5 in the presence of ascorbic acid and the solution then titrated with dithizone as for zinc determination. For the separate determination of Cu, Zn, and Pb, an aliquot was then taken containing 10 – 25 γ of "total metals". The chosen solution was neutralized with ammonia to an approximately neutral or weakly acid reaction, when it was diluted with an approximately equal volume of 0.10 – 0.20 N HCl, and 2 ml of a 25% ascorbic acid solution added. In the acid extracts one often came across appreciable amounts of iron, for complexing which, large amounts of citrate were required, and even this did not always prevent oxidation of the dithizone. Moreover, we found that copper, in the presence of citrate, is very slowly extracted from acid solution by dithizone. It was found that ascorbic acid while reducing Fe^{3+} to Fe^{2+} did not interfere at all with the extraction of copper, and prevented dithizone from being accidentally oxidized during titration. Copper was titrated with dithizone, the latter being standardized against zinc in an alkaline medium, and against copper in an acid medium. After the determination and simultaneous separation of copper, the aqueous solution containing Zn and Pb was adjusted to a pH of 8 to 8.5 with ammonia (established by withdrawing an aliquot for test or from the change in color of iron ascorbate present in the solution), and the zinc and lead were then determined as described above.

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*An empirical value determined during hydrochemical exploration by titrating a sample of water in a weakly alkaline medium with dithizone. In samples of water taken in territories where polymetallic ore deposits are found, this value generally reflects the zinc content.

It is obvious from Table 1 that the optimum pH limits for the re-extraction of lead by thiosulfate are 5.5 – 6.0.* At higher pH values, lead is not extracted completely, while at lower values zinc is also re-extracted to some extent with the lead.

b) Separation of the Carbamates of Copper, Lead, and Zinc by Re-extraction with Hydrochloric Acid. To the test sample of water was added 10 ml of 5 N $CaCl_2$ purified with dithizone, 2 ml of 5% sodium diethyldithiocarbamate solution, and 10 ml/liter of a saturated solution of ammonium citrate, and the pH of the solution adjusted to 8.5 – 9 (phenol red or thymol blue). 15 ml of carbon tetrachloride was then added and the whole shaken vigorously for 5 minutes. The volume of test water was 0.5 liter or less.** After standing, the CCl_4 layer was transferred to a small separating funnel. Colorimetric measurements were carried out on the colored copper complex immediately, or after re-extraction of zinc and lead. Zinc was re-extracted by shaking four times with 5 ml lots of 0.1 N HCl for 1 minute periods. In the combined re-extracts (or an aliquot part) zinc was determined as in a) by extraction titration with dithizone.*** The carbon tetrachloride which then only contained copper and lead carbamates was washed with "metal-free" water for removal of residual copper and lead carbamates; lead was then re-extracted from it by shaking it twice, for 1 minute each time with 5 ml lots of 3 N HCl. It is extremely important to use acid free from traces of metals. Normally zinc is present in the commercial acid (even the best grade) and this increases the results for lead sharply. Naturally, both during the zinc determination (after re-extraction with 0.1 N HCl), and, particularly, during the lead determination, it is essential to introduce corrections by carrying out a blank. Acid of the requisite normality (particularly for re-extraction of lead) is best prepared from acid distilled by the "cold method" [7]. Ammonia solution can be prepared from the commercial solution by adding solid alkali to the latter, and then passing the gaseous ammonia liberated through twice-distilled water cooled with ice.

The re-extract containing the lead is neutralized with ammonia to the phenol-red endpoint and the lead then determined as indicated in a).

It is clear from Table 2 that there is a good separation of copper, zinc, and lead. Only in the case of very low amounts of lead (2 – 4 γ) is there observed appreciable increases (up to 100%) in the results for lead as a result of inclusion of traces of zinc. When, however, potassium cyanide is used, low results are obtained as shown by results which we obtained and by published results [1, 3].

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* A purified solution of thiosulfate will keep its pH unchanged for a long time as long as it is not acidified. Accordingly, having established the amount of acid (usually 1 – 3 drops of 0.01 N HCl per 50 ml of $Na_2S_2O_3$) necessary, there is no need to use the pH-meter further.

** The amounts of the acid extracts (which normally contained large amounts of micro elements) taken were such that they contained 10 – 100 γ ΣM, and the amount of $CaCl_2$ was reduced proportionally. The diethyldithiocarbamate solution was added after neutralization of the acid and complexing of the iron.

*** For an initial volume of test water of 0.5 – 1 liter, the results for zinc is multiplied by 1.2. For volumes up to 100 ml there is no need for a correction.

TABLE 2

Determination of Cu, Zn, and Pb After Re-extraction of Zn and Pb Carbamates From a Layer of CCl_4

Cu γ/l		Zn γ/l		Pb γ/l		Cu γ/l		Zn γ/l		Pb γ/l	
taken	found	taken	found	taken	found	taken	found	taken	found	taken	found
5	5	5	5	5	6	20	20	30	28	10	11
10	9	10	10	10	9	10	10	20	19	2	4
20	20	20	22	20	18	—	—	50	48	4	7
30	30	45	40	5	4	10	10	50	49	4	5
40	40	40	36	40	40	50	50	50	48	4	4
2	2	2	2	2	2						

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* The extraction of the total carbamates of metals was carried out in the first six experiments from one liter of solution, and in the remaining experiments, from 1.5 liters. The re-extraction of zinc was done with 0.1 N HCl and re-extraction of Pb was done with 3 N HCl.

SUMMARY

A method has been developed for the quantitative separation of lead from a mixture of the dithizonates of zinc and lead (after separating copper in the usual way) by treatment with thiosulfate at a pH of 5.5 – 6.0. The re-extracted lead is determined by titration with dithizone at a pH of about 8.5.

A method has been developed for the separate determination of copper, zinc and lead diethyldithiocarbamates by treatment with HCl solutions of different concentrations, and subsequent titration with dithizone.

The two methods do not require the use of potassium cyanide and are suitable for field geochemical work.

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SEPARATION OF TITANIUM FROM ACCOMPANYING ELEMENTS BY ION EXCHANGE CHROMATOGRAPHY

COMMUNICATION 3. SEPARATION OF TITANIUM AND ZIRCONIUM[*]

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In order to establish the possibility of carrying out a chromatographic separation of quadrivalent titanium and zirconium, a study was made of their sorption by ion exchange resins from hydrochloric acid solutions. The use of hydrochloric acid solutions in chromatography is interesting from the point of view of anion and cation exchange, since, very often, a small change in the acid concentration can lead to a significant difference in the sorptive capacity, even of elements with very similar properties [1 – 8].

The sorptive capacity of the elements has been studied by many different methods (by analysis of the solution flowing out of the column, by determining the distribution of an element on the column, etc.). A method which is convenient and simple enough, in our opinion, is the method of determining partition coefficients, this consists of shaking an accurately known amount of the air-dry resin until equilibrium is reached with a known volume of test solution, an aliquot of the solution is then taken and the amount of the element which has not been adsorbed on the resin determined. The distribution coefficient φ is calculated by means of the formula [9]:

$$\varphi = \frac{M_1}{M-M_1}\,\frac{V}{m}$$

where M_1 is fraction of the element in the resin in milligrams; M is the total amount of the element contained in the original solution, in milligrams; V is the volume of solution; and m is the weight of the resin.

As in previous work, we determined the comparative sorption of these elements by this method. In our experiments V and m were kept constant at 60 ml and 0.5 g, respectively. The concentration of the quadrivalent titanium solution was 1.49×10^{-4} mole/liter, while that of the zirconium was 8.97×10^{-5} mole/liter. The ion exchange resins tested were the cation exchange resins SBS, KU-2 and the anion exchange resins EDE-10 and AN-2F. The resins were washed free from impurities before use; SBS and KU-2 were converted into the H-form while EDE-10 and AN-2F were converted into the Cl-form. The titanium concentration of the equilibrium solutions was determined photometrically by means of chromotropic acid, while the zirconium concentration was determined by means of arsenazo.[**]

It was established that neither titanium nor zirconium is sorbed by the anion exchange resins from 0.1 – 6 N solutions of hydrochloric acid. The results obtained with the cation exchange resins are given in Table 1.

It follows from Table 1 that, in comparatively dilute hydrochloric acid solutions (0.1 – 1 N), zirconium is completely sorbed by both cation exchange resins. This indicates that, under the given conditions, zirconium exists in solution as positively charged ions. At higher acid concentrations there is observed some difference in the sorption of the element by the cation exchange resins: SBS, though only to a negligible extent, still does

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[*] Communication 2, See J. Anal. Chem. 12, 377 (1957).

[**] Benzene-2-arsonic-acid <1-azo-2> 1,8-dihydroxynaphthalene-3,6-disulfonic acid.

TABLE 1

Partition Coefficients for Quadrivalent Titanium and Zirconium in Hydrochloric Acid Solutions on SBS and KU-2

Normality of HCl solution	SBS		KU-2	
	φ_{Ti}	φ_{Zr}	φ_{Ti}	φ_{Zr}
0,1	216,0	Completely absorbed	713,8	Completely absorbed
1	10,3	•	Not absorbed	•
2	Not absorbed	116,0	•	56,3
4	•	17,4	•	Not absorbed
6	•	11,2	•	•

TABLE 2

Chromatographic Separation of Titanium and Zirconium on KU-2 by Means of Hydrochloric Acid

Ratio Ti : Zr	Ti taken, in mg	Volume of 1 N HCl, in ml	Ti found, in mg	Zr taken, in mg	Volume of 4 N HCl, in ml	Zr found, in mg
1000 : 1	200,0	400	201,0	0,200	50	0,198
1000 : 1	200,0	400	200,0	0,200	50	0,196
1 : 1	1,000	150	0,999	0,997	100	0,990
1 : 1	1,000	150	1,000	0,997	100	0,992
1 : 1	1,000	150	0,990	0,997	100	0,986
1 : 100	0,050	150	0,050	5,000	175	4,942
1 : 100	0,050	150	0,050	5,000	175	4,983
1 : 10000	0,005	75	0,005	50,16	200	50,14
—	0,005	75	0,005	50,16	200	50,13

sorb Zr from comparatively acid solutions. Sorption of titanium in the HCl concentration range 0.1 – 1 N is low and does not occur in more acid solutions. This, presumably, cannot be explained by formation of anionic complexes, since no sorption of this element by the anion exchange resins was observed.

Differences in the sorption of titanium and zirconium in 1 N HCl gave us a basis for developing the following method for separating these elements. A column (11 cm long and 0.5 cm in diameter) was filled with KU-2 resin in the H-form and the resin washed with 1 N HCl; the test solution containing titanium and zirconium chlorides, and 1 N with respect to HCl, was then introduced into the column. The column was washed with 1 N HCl until all the titanium had been extracted; the zirconium was eluted with 4 N HCl. Results of such separations are given in Table 2.

The results of these separations can be regarded as satisfactory. Reactions for zirconium in the titanium solutions, and for titanium in the zirconium solutions gave negative results. SBS cannot be recommended for separating these elements, since, in the first instance, for elution of equal amounts of titanium, approximately 2.5 times more 1 N HCl is required, while, secondly, 4 N HCl elutes only 80 – 85% of the zirconium from this resin.

SUMMARY

1. The partition coefficients of quadrivalent titanium and zirconium between the ion exchange resins SBS and KU-2, and hydrochloric acid solutions of various concentrations have been determined. It has been established that these elements are not sorbed from 0.1 – 6 N hydrochloric acid solutions by the anion exchange

resins EDE-10 and AN-2F.

2. A method has been developed for the quantitative chromatographic separation of titanium and zirconium at ratios of Ti:Zr from 1000:1 to 1:10,000 by means of a hydrochloric acid solution on the cation exchange resin KU-2.

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DETERMINATION OF DI- AND TRIVALENT TITANIUM IN CHLORIDE MELTS BY MEANS OF FERRIC CHLORIDE

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Detailed study of the electrolysis of salt melts containing titanium necessitates the separate determination of di- and trivalent titanium in the electrolyte. Existing methods for the determination of titanium in low valency states [1, 2] do not always give satisfactory results. In several instances it is of interest to determine the valency states of titanium directly in the salt melt, without cooling it and getting the titanium into solution.

The most suitable approach seemed to be oxidation of di- and trivalent titanium directly in the salt melt by ferric chloride, with parallel determination of trivalent titanium in an aqueous solution of the electrolyte. This approach would permit separate determination of the amount of Ti^{II} and Ti^{III} in each others presence. Nevertheless, this method also is complicated by the thermal dissociation of ferric chloride, and by its volatility [3].

At high temperatures $FeCl_3$ decomposes appreciably. Accordingly, it was found expedient to fuse the test samples, not with pure ferric chloride, but with solutions of ferric chloride in alkali metal chlorides.

Preparation of Melts of Ferric Chloride with Alkali Metal Chlorides

Anhydrous ferric chloride free from $FeCl_2$ was prepared by chlorination of Armco iron at 450 – 500 deg. Subsequently $FeCl_3$ was fused with the chlorides of the alkali metals (a eutectic mixture of KCl + LiCl) at 450 – 500 deg in a stream of chlorine.

At concentrations below 5 – 6% of $FeCl_3$ a homogeneous melt having the color of strong tea was obtained. At higher concentrations, a second liquid phase separated out on the bottom of the test tube.

Table 1 contains results of several experiments in which a eutectic mixture of lithium and potassium chlorides was fused with 10 and 30% of $FeCl_3$ at 500 deg. The fused salts were kept in a liquid state in a chlorine atmosphere for about 5 minutes, and then rapidly cooled. The top and bottom layers which differed sharply from each other in color were analyzed for their contents of $FeCl_3$ and $FeCl_2$ (Table 1).

TABLE 1

$FeCl_3$ added, in % wt.	Found, in % wt.			
	In the top layer		In the bottom layer	
	$FeCl_3$	$FeCl_2$	$FeCl_3$	$FeCl_2$
10	5,1	0,12	65,0	None
10	5,74	0,10	65,3	″
30	6,2	0,11	65,3	″

As the results show, the bottom layer of the fused salts is a phase with a constant composition approximating to that of the compound $KFeCl_4$. The fusion temperature of this phase was 260 ± 2 deg. Microscopic examination showed that no crystals of $FeCl_3$, KCl, or LiCl were present in the congealed lower layer of the fused salts. Obviously, this phase is a solution of KCl in $KFeCl_4$. The yellow anisotropic crystals which made up this phase had a refractive index $n > 1.567$. The top layer of the fused salts was a saturated layer of $KFeCl_4$; after cooling, individual crystals of a second phase of $KFeCl_4$, LiCl, and KCl were found in it under the microscope. It should be pointed out that formation of layers was only observed in the fused mixtures of $FeCl_3$ with LiCl +

KCl; it did not occur in the systems: $FeCl_3$ + NaCl [4], $FeCl_3$ + LiCl, and $FeCl_3$ + KCl (we studied the last two systems). Ferrous chloride which is formed as the result of partial thermal dissociation of $FeCl_3$ concentrated only in the top layer of the melt. This shows that $FeCl_2$ does not dissolve in $KFeCl_4$.

The compound $KFeCl_4$ is more stable to thermal dissociation than ferric chloride. This confirms experiments in which $KFeCl_4$ was held for a definite time in a fused state at 500 deg under an atmosphere of pure argon, and, after rapid cooling, was analyzed for its content of ferrous chloride. Results of these experiments are shown in Table 2; for comparison, results of experiments with a melt containing 8% wt of $FeCl_3$ are included.

As these results show, $FeCl_3$ dissolved in the melt KCl + LiCl broke down more rapidly.

Nevertheless, keeping melts containing ferric chloride for a long time at high temperatures can lead to formation of appreciable amounts of $FeCl_2$, and can therefore lead to incorrect results.

TABLE 2

$KFeCl_4$			Melt, containing 8% wt. of $FeCl_3$ in KCl + LiCl		
Time for which melt was kept at 500°, in min.	$FeCl_2$ found in % wt.	$FeCl_2$ decomposed, in % wt.	Time for which melt was kept at 500°, in min	$FeCl_2$ found, in % wt.	$FeCl_2$ decomposed in % wt.
5	0,006	0,013	4	0,05	0,74
10	0,011	0,022	8	0,06	0,95
15	0,018	0,036	15	0,065	1,02
—	—	—	25	0,10	1,55

When ferric chloride, in the form of the compound $KFeCl_4$ prepared beforehand, is added to the melt in amounts which are only slightly in excess of that required for oxidizing lower valency titanium, and the melt is then rapidly cooled, it is possible to reduce the formation of $FeCl_2$ to a minimum.

Determination of the Amount of Di- and Trivalent Titanium. Below is given a brief description of a method for the determination of di- and trivalent titanium in fused chloride electrolytes.

A sample of the melt was taken and cooled in an inert atmosphere (argon) and then transferred to a Γ-shaped tube. Some $KFeCl_4$ prepared beforehand was placed in a sideshoot of this tube; the amount of $KFeCl_4$ taken should not be more than 1.5 to 2 times the amount necessary for complete oxidation of Ti^{II} and Ti^{III} to Ti^{IV}. The tube was then hermetically sealed, evacuated and filled with pure argon, and its lower end — containing the test material — placed in the heating oven. The sideshoot containing the $KFeCl_4$ should be outside the oven in a cold zone. After the sample had fused, the $KFeCl_4$ was thrown into it by inclining the tube; the tube was then vigorously shaken in order to mix the contents; after mixing the tube was withdrawn from the oven and cooled as rapidly as possible to room temperature. The sample was weighed and dissolved in water, the solution was acidified with H_2SO_4 or HCl (10%). Ferrous iron was determined in the aqueous solution (in mg equivalents per g of sample taken).

TABLE 3

No. of replicates	Ti^{2+} % wt., determinod by fusion with Fe^{3+} according to equation (1)	Ti^{3+} % wt., calculated by means of equation (2) on the basis of the fusion reaction	Ti_{total} % wt., calculated as the sum of di- and trivalent titanium	Ti_{total} % wt. determined by dissolution in water and by titration with $FeCl_3$	Relative error, in %
1	4,95	0,67	5,62	5,62	0,04
2	4,92	0,71	5,62	5,62	0,07
3	4,88	0,74	5,62	5,62	0,09
4	2,23	—	2,23	2,23	0,09
5	2,23	—	2,23	2,23	0,09

A second sample was taken from the test melt, and, after cooling to room temperature in an inert atmosphere, was dissolved in dilute H_2SO_4 or HCl (10%). Trivalent titanium (in mg equivalents per g of sample taken) was then determined in the aqueous solution.

Assume that n mg. equivalents of Fe^{II} was found per g of test sample by fusion with $FeCl_3$, and that m mg. equivalents of Ti^{III} per g of sample was found in the aqueous solution, then the original melt will contain:

$$a = 11{,}88\,(n - m)\ \text{Wt. \%}\ TiCl_2. \qquad (1)$$

$$b = 15{,}43\,(2m - n)\ \text{Wt. \%}\ TiCl_3. \qquad (2)$$

As examples, Table 3 contains results of the analysis of chloride melts, in which titanium was introduced by electrolysis with an anode consisting of titanium oxide (TiO), or by the interaction of dry hydrogen chloride with the metal in the melt.

SUMMARY

1. A method is described for obtaining melts of $FeCl_3$ with alkali metal chlorides, in which thermal decomposition of ferric chloride is reduced to a minimum.

2. A technique is described for the separate determination of di- and trivalent titanium in salt melts by means of ferric chloride which is added to a sample of the test melt in the form of the compound $KFeCl_4$ prepared beforehand.

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DETERMINATION OF SMALL AMOUNTS OF ZIRCONIUM AND HAFNIUM IN SILICATE ROCKS

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All rocks and minerals which contain zirconium usually contain hafnium as well [1 – 2]. As a result of of the extremely close similarity in the chemical properties of these two elements, sufficiently accurate methods for their quantitative separation are not yet known. As a result of this they are separated together, and the content of each element in the concentrates thus obtained, is determined either by optical spectroscopy [3], or by X-ray spectrographic methods [4].

All the same, during the separation of zirconium and hafnium from silicates rocks by published methods, it has been found that complete separation of the elements is not achieved by any of these methods, when the total content of zirconium and hafnium is less than 0.01%. Evaluation of the applicability of each of the methods for separating zirconium and hafnium from silicate rocks was carried out as follows. To a finely ground sample of granite free from zirconium and hafnium, was added a known amount of a solution of one of the elements and the requisite amount of a solution of the radioisotope of the same element; the mixture was then broken down with a mixture of hydrofluoric and sulfuric acids (or with a mixture of hydrofluoric and perchloric acids). From the solutions obtained in this way, zirconium and hafnium were precipitated as phosphates, arsenates, mandelates, phenylarsonates, and 4-dimethylaminoazobenzene-4^1-arsonates. The precipitates were calcined and completeness of separation of zirconium and hafnium checked radiometrically. It follows from the results obtained that for a total content of zirconium and hafnium in the tested silicates less than 5×10^{-2}%, their separation in the form of phosphates and arsenates is already incomplete. Quantitative separation of zirconium and hafnium as mandelates under the conditions recommended by Mills and Herman [5] is only possible for a total content of both elements in the silicate rocks of not less than 2×10^{-2}%.

Precipitation with phenylarsonic acid according to the technique developed by Alimarin and Medvedeva [6] ensures complete separation of zirconium and hafnium from silicate rocks containing not less than 1×10^{-2}% of the total.

Decomposition of the sample with a mixture of HF and $HClO_4$ instead of HF and H_2SO_4, and the use of hydrochloric acid for dissolving the residue after decomposition instead of sulfuric acid, favors more complete deposition of the phenylarsonates of zirconium and hafnium. It was also found that by simply increasing the amount of added phenylarsonic acid, it is possible to ensure complete separation of both elements for their total content in silicate rocks of down to 1×10^{-4}%, even from sulfuric acid solutions. All the same, the concentration of zirconium and hafnium achieved under such conditions still proved insufficient (Table 1), as a result of which, the zirconium in the concentrates obtained, in view of its low content, was determined by the X-ray spectrographic method with a large error, while hafnium could not be detected at all. The use of an X-ray spectrographic method for determination of zirconium and hafnium in the concentrates obtained has the advantage that the experimental accuracy in the given instance is independent of the bulk composition of the sample (as is true in optical spectroscopy). The technique applied [4] permits determination of zirconium and hafnium, for contents of these elements in the test sample greater than 0.5 and 0.05% respectively. 3 – 5 mg of test concentrate is sufficient for a determination.

TABLE 1

Composition of the Concentrates Obtained After Calcining Phenylarsonate Precipitates. Sample of Rock 7 — 10 g (according to X-ray spectrographic results)

Element	Content (in %) in the concentrate		Element	Content (in %) in the concentrate	
	After the first precipitation	After the second precipitation		After the first precipitation	After the second precipitation
Ti	10	>10	Ca	0,1—0,5	Not detected
Zr	0,5—1,5	0,7—2	Ba	0,1	»
Fe	0,1—1	0,1—0,5	Zn	0.007—0,08	0,007—0,01
Al	0,1—1	0,05—0,1	Gu	0,005—0,01	0,005
As	0,1—1,5	0,1—1	Mn	0,001—0,005	0,005
Pb	0,1—1	0,001—0,005	Sn	0,001—0,005	Not detected
Mg	0,1	Not detected	Hf	Not detected	»

Repeated reprecipitation with phenylarsonic acid makes it possible to lower the weight of the concentrate separated from 10 g of silicate rock from 50 — 70 to 38 — 50 mg. The zirconium content after reprecipitation amounts to 0.7 to 2.0%; the hafnium content, however, still cannot be determined with sufficient accuracy(Table 1).

TABLE 2

Distribution of Hf^{181} During the Concentration of Zr and Hf from Silicate Rocks

Content in the rock, in %		Hf^{181} found, as a % of that introduced		
Zr	Hf	In the first filtrate	In the second filtrate	In the concentrate
$1{,}4\cdot10^{-2}$	$3{,}0\cdot10^{-4}$	0,8	2,0	97,2
$1{,}2\cdot10^{-2}$	$2{,}8\cdot10^{-4}$	0,4	1,3	98,2
$8{,}4\cdot10^{-3}$	$1{,}9\cdot10^{-4}$	1,6	3,7	94,5
$3{,}3\cdot10^{-3}$	$1{,}0\cdot10^{-4}$	1,6	1,8	96,6
$2{,}6\cdot10^{-3}$	$5{,}5\cdot10^{-5}$	1,5	4,7	94,0

When the concentrate obtained by precipitation with phenylarsonic acid is repeatedly reprecipitated by means of 4-dimethylaminoazobenzene-4^{1}-arsonic acid,which forms less soluble precipitates with zirconium and hafnium [7 — 9], it is possible, under suitable chosen conditions, to decrease the weight of the concentrate to 3 — 5 mg; the zirconium content of such a concentrate increases to 10 — 66%, while that of hafnium becomes 0.2 — 1.5%. The distribution of Hf^{181} during the concentration of zirconium and hafnium from silicate rocks by the procedure outlined below is shown in Table 2.

The distribution of Zr^{95} during concentration of zirconium and hafnium from the same rocks is identical to the distribution of Hf^{181}; of the Zr^{95} introduced, on an average,96.8% was found in the concentrates isolated.

The concentration technique consists of the following. 5 — 10 g of finely ground rock is decomposed in a platinum basin with a mixture of hydrofluoric and perchloric acids (or with a mixture of hydrofluoric and sulfuric acids). After the sample has been broken down completely and Hf has been removed, the residue is dissolved in 50 ml of 2 N HCl and the normality of the acid lowered to 1 N by dilution with water; 1 — 2 ml of 30% hydrogen peroxide is added (for masking titanium) followed by 5 — 6 ml of a 20% solution of phenylarsonic acid to precipitate zirconium and hafnium. The precipitate should be allowed to stand for at least 24 hours before filtering, it is then washed with a 0.1% solution of phenylarsonic acid in 0.1 N HCl, and dried, and finally calcined for 1.5 — 2 hours at 900 — 1000 deg. The dioxides of zirconium and hafnium obtained by calcining their phenylarsonates are fused with potassium pyrosulfate, and the melt dissolved in 50 ml of 6 N HCl; the whole is heated on a water bath for 10 – 15 minutes. After cooling, 1 – 2 ml of 30% hydrogen peroxide is added, followed by 5 ml of a 2% solution of sodium 4-dimethylaminobenzene-4^1-arsonate, 30 – 35 ml of water, and 10 ml of 1% methyl orange solution, which is one of the components of the organic coprecipitant [10] favoring more complete separation of zirconium and hafnium. Instead of methyl orange one can use any sulfonic acid which has a sufficiently high molecular weight, for example, β-naphthalenesulfonic acid, α-anthraquinonesulfonic acid, etc. After 24 hours, the precipitate formed is filtered, washed 2 – 3 times with a 0.1% solution of 4-dimethylaminobenzene-4^1-arsonic acid in 0.1 N HCl, dried, and then calcined at 900 – 1000 deg. The zirconium and hafnium content of the concentrate obtained in this way is determined by an X-ray spectrographic method.

The use of the radioactive isotopes Zr^{95} and Hf^{181} for establishing the completeness of the separation of zirconium and hafnium from silicate rocks, has shown that fairly complete separation of both elements is possible when their total content in the rocks is not less than 1 × 10^{-4}%.

The method which has been developed has been tested for separating zirconium and hafnium from rocks of the Verkh-Isetskii intrusion, for subsequent X-ray spectrographic determination of each of these elements [11].

In conclusion, we should like to thank I. D. Shevaleevskii for carrying out all determinations of zirconium and hafnium in the concentration obtained by the X-ray spectrographic method.

SUMMARY

A method has been developed for concentrating zirconium and hafnium from silicate rocks containing a total amount of these elements ranging from 0.5 to 1 × 10^{-4}%. The method consists of their precipitation with phenylarsonic acid, and subsequent reprecipitation with 4-dimethylaminoazobenzene-4^1-arsonic acid. Recovery of each element is 94 – 100%. As a result of this high degree of concentration, it is possible to determine the content of each element with reasonable accuracy by the X-ray spectrographic method.

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PHOTOMETRIC DETERMINATION OF GERMANIUM BY MEANS OF 9-[p-(N-DIMETHYLAMINO)] -PHENYL-2, 3, 7-TRIHYDROXY-6-FLUORONE

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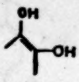
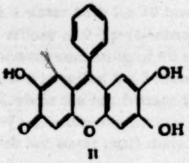
Among those organic reagents known at present for germanium, an important place is occupied by compounds containing the ortho-dihydroxy group [1] in their molecules



The most interesting of such organic compounds is 9-phenyl-2, 3, 7-trihydroxy-6-fluorone (II), which was suggested for the determination of germanium by Giles in 1947 [1].



II

Thanks to its high sensitivity and specificity, phenylfluorone has found wide application in the analytical chemistry of germanium.

On addition of traces of germanium to solutions of phenylfluorone in dilute hydrochloric or sulfuric acid, there is observed a change in the color of the solution from yellow to orange, as a result of the separation of the raspberry-colored precipitate of the germanium-phenylfluorone compound.

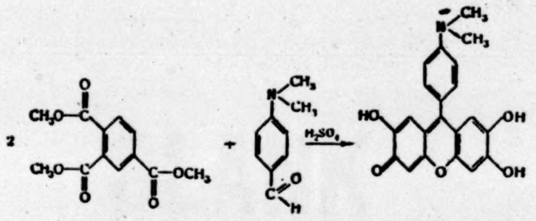
The fact that the product formed by the interaction of germanium with phenylfluorone separates out as a solid phase presents serious difficulties for the use of this reagent for the photometric determination of germanium, such a determination being, accordingly, only possible in the presence of stabilizing agents in solution. Thus, Cluley [2] using gum arabic managed to prepare stable sols of the phenylfluorone compound of germanium with contents of up to 20 γ of GeO_2 in 1 ml of solution. Cluley's method has not found wide application in the Soviet Union because of the nonavailability of gum arabic. Attempts have been made to use gelatine instead of gum arabic [3]. Using gelatine, we were only able to get stable sols of the germanium-phenylfluorone compound in very dilute solutions containing not more than 0.2 γ GeO_2 in 1 ml. In addition, the reproducibility of the color intensity of the solutions proved to be far from satisfactory, particularly in more concentrated germanium solutions, since in the presence of gelatine, even when the conditions used were kept strictly identical, it was difficult to prepare suspensions of the germanium-phenylfluorone compound with equal degrees of dispersion (on which the intensity and shade of the color of the solution mainly depends).

It would be more expedient to change the properties of the reagent itself in such a way that the product obtained, while preserving the sensitivity and specificity of phenylfluorone, formed soluble compounds witl germanium. One approach to solving this problem appeared to be the introduction of basic groups into the phenylfluorone molecule.

In the course of the work described here,an analog of phenylfluorone containing a basic substituent was synthesized, this compound was: 9[p-(N-dimethylamino)]phenylfluorone; conditions were also established for the photometric determination of germanium by this new reagent.

Synthesis of 9-[p-N-dimethylamino)]-phenylfluorone

Synthesis of 9-[p-(N-dimethylamino)] phenylfluorone can be carried out in a similar fashion to that of phenylfluorone, the only difference is the use of N-dimethylaminobenzaldehyde instead of benzaldehyde; p-N-dimethylaminobenzaldehyde is condensed with triacetylhydroxyquinone in the presence of concentrated sulfuric acid according to the scheme:



18 g (0.072 M) of freshly prepared triacetylhydroxyhydroquinone and 5 g (0.035 M) of p-dimethylaminobenzaldehyde are dissolved on heating in a mixture of 80 ml alcohol, 80 ml water, and 8 ml of concentrated sulfuric acid. The solution obtained is boiled on a water bath for 10 hours, and is then kept for 10 hours at room temperature. The orange-red precipitate of the sulfate of 9-[p-(N-dimethylamino)] phenylfluorone which is formed, is filtered off, and then dissolved in a mixture consisting of 80 ml of alcohol, 80 ml of water and 8 ml of concentrated sulfuric acid. The solution obtained is boiled for 5 minutes with a small amount of activated charcoal, after which the charcoal is filtered off, while the hot filtrate is neutralized with ammonia to a pH of approximately 7; a red precipitate of the base 9-[p-(N-dimethylamino)] phenylfluorone thereupon separate out. The latter is filtered while hot, and is washed with hot water until there is complete absence of any smell of ammonia.

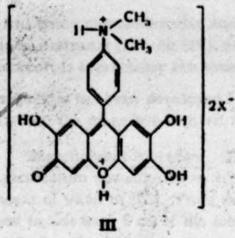
9-[p-(N-dimethylamino)]phenylfluorone is a red microcrystalline powder with a greenish tinge, and has a melting point higher than 300 deg; it is insoluble in water and in most organic solvents. It dissolves readily in alkalis to form raspberry-red solutions. It dissolves in mineral acids on heating, or in the presence of alcohol.

Yield 66 g (52%). Found in %: N 3.73; 3.75. Calculated %: N 3.85.

Henceforth we shall denote 9-[p-(N-dimethylamino)]phenylfluorone by DAPhF, while its compound with germanium will be denoted by germanium-DAPhF compound.

Photometric Determination of Germanium by Means of 9-[p-N-dimethylamino)]-phenylfluorone

Conditions for the photometric determination of germanium by means of DAPhF were established for the case of hydrochloric acid solutions, since such solutions are prepared in the course of analysis. DAPhF forms salts with acids by means of their amino- and oxonium groups (III). The most stable solutions of DAPhF were those obtained in the case of dilute hydrochloric acid solutions ($C < 1N$); in more concentrated hydrochloric acid solutions, on standing, a yellow crystalline precipitate separated out, presumably, as the result of the formation of a sparingly soluble salt through the oxonium oxygen. In weakly acid media, the possibility of the formation of oxonium salts is limited on account of the greater tendency to hydrolyze, and DAPhF is kept in solution thanks to the readily soluble salt it forms through the amino nitrogen. With increasing temperature,the stability of DAPhF solutions increases because of the increasing solubility of its oxonium salt.



III

In the presence of germanium, the yellow color of DAPhF solutions changes to orange; under these conditions, the maximum of the color intensity is only observed on addition of a large excess of reagent. This indicates a low stability for the germanium – DAPhF compound formed, this being determined, presumably, by an increase in the basic properties of the reagent as a result of the introduction of the basic amino group into its molecule.

It has been established that maximum color stability of the solutions of the germanium-DAPhF compound is achieved on addition of 2 ml of a 0.5% solution of DAPhF per 8 ml of the test solution containing from 0.5 to 1.0 γ of GeO_2 in 1 ml.

Solutions of the germanium-DAPhF compound show an appreciable opalescence when examined in ultraviolet light–this indicates their colloidal character; nevertheless, the presence in the molecule of the compound of a basic dimethylamino group communicates to the sols stability in acid media.

In dilute hydrochloric acid (1 N), solutions of the compound of germanium with DAPhF, for contents of the germanium of 1.2 γ GeO_2 in 1 ml, are stable enough without addition of any stabilizing agents. With increasing acidity of the solution, the stability of the sols of the germanium-DAPhF compound decreases as the result of the formation of the oxonium salt.

Solutions of the germanium-DAPhF compound are highly dispersed colloidal systems and fully conform to the Lambert – Beer law at low germanium concentrations ($c < 1\gamma$ GeO_2/ml). The deviations from this law which are observed at higher germanium concentrations, are related, apparently, to a decrease in the dispersivity of the system (Fig. 1).

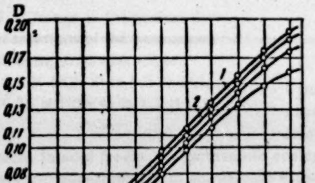


Fig. 1. Relation between the optical density of solutions of the germanium – DAPhF compound and the germanium concentration: 1) In 0.2 N HCl; 2) in 0.5 N HCl; 3) in 0.7, 0.9, 1.0 and 1.1 N HCl; 4) in 1.18 N HCl (t = 22 deg).

The curves shown in Fig. 1 show that the value of the optical density of solutions of the germanium – DAPhF compound falls with increasing acidity of the medium.

Temperature affects the value of the optical density of the colored compound of germanium (Curves in Fig. 2); with decreasing temperature the value of the optical density of solutions of the germanium – DAPhF compound increases appreciably. Changes in the color of solutions of the germanium – DAPhF compound, determined by temperature variations, are completely reversible: on returning to the original temperature conditions, the intensity of the color of the solutions is rapidly and completely restored.

At a constant temperature, the color of solutions of the germanium – DAPhF compound in weakly acid media remains stable for several hours. The maximum color intensity is obtained in 0.5 – 1.5 hours, depending on the acidity of the solution (Fig. 3).

Measurements of the optical density of the solutions were carried out on a FEK-M photocolorimeter using a green filter having a transmission region at 600 – 580 mμ.

The sensitivity of the determination amounts to 0.05 γ GeO_2 in 1 ml of test solution.

Arsenic and bismuth present in the solutions being photometrically measured have no effect on the germanium determination. Under similar conditions, antimony (III), tin (IV), and molybdenum react with DAPhF, but the sensitivity of the reagent with these elements is appreciably less than with germanium.

As the result of work we carried out, a technique has been developed for the photometric determination of small amounts of germanium by means of DAPhF; the procedure is given below.*

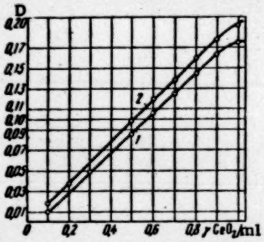


Fig. 2. Effect of temperature on the optical density of solutions of germanium – DAPhF compound 1) 23°; 2) 16°.

Experimental Procedure. The test hydrochloric acid solution of germanium was adjusted to 0.75 – 1 N by addition of the necessary amount of water or HCl. From the hydrochloric acid solution prepared in this way, 8 ml of the solution was pipetted into a small graduated tube, the germanium content in the given volume being less than 10 γ GeO_2. When the test solution contained more germanium, a smaller aliquot was taken and the volume made up to 8 ml with 0.9 N HCl. 2 ml of a 0.05% solution of DAPhF was added and the whole mixed and left to stand in the dark for one hour.**

The optical density was measured with a green filter, using a cell with a layer thickness of 10 mm. The reference solution was an identical solution containing all the reagents apart from germanium. The germanium content was established by means of a calibration curve.

A calibration curve was constructed by measuring out from 0.1 to 1 ml of a stock solution of germanium containing 10 γ GeO_2 in 1 ml, into test tubes, and making the volume up to 8 ml with 0.9 N HCl in each case. 2 ml of reagent solution was added to each test tube, and, after standing for one hour, the optical density was measured.

It is essential that the construction of a calibration curve and determination of germanium should be carried out under the same temperature conditions.

The authors wish to thank N. Ia. Postovskii for his valuable advice during the work described here.

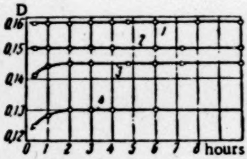


Fig. 3. Change in the optical density of solutions of the germanium–DAPhF compound with time: 1) In 0.2 N HCl; 2) in 0.5 N HCl; 3) in 0.75 N HCl; 4) in 1.2 N HCl.

SUMMARY

The synthesis of 9-[p-(N-dimethylamino)]phenyl-2, 3, 7-trihyroxy-6-fluorone – a reagent for germanium – is described. The advantages of 9-[p-(N-dimethylamino)]phenylfluorone over phenylfluorone is that solutions of the germanium compound of the former are stable in acid media, for germanium contents up to 1.2 γ GeO_2 per ml, and that this reagent can be used for photometric determination of germanium without having to use special stabilizing agents. A method has been developed for the photometric determination of germanium using the reagent mentioned above.

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* After completion of the work described here we became aware, via a reference article, of an article by some Japanese workers: Kenjero Kimura, Kazuo Saita, Masaka Asada published in Chem. Abstracts 51, No. 1, 125 (1957), in which 9-[p-(N-dimethylamino)] phenylfluorone was described as a reagent for germanium. Information regarding the use of this compound for the quantitative determination of germanium was not given in the reference.

** Preparation of DAPhF solution: 0.5 g of the reagent was dissolved in 50 ml of 0.9 N HCl on heating at 60 – 70 deg. and the volume made up to 100 ml with alcohol.

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DETERMINATION OF VANADIUM AND CHROMIUM BY PHOTOMETRIC TITRATION

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The method most widely used for the determination of vanadium and chromium in alloyed steels, and of vanadium in ferrovanadium, is titration with Mohr's salt using phenylanthranilic acid as indicator [1]. Nevertheless, during the determination of vanadium in steels containing large amounts of chromium or nickel, visual fixing of the endpoint becomes difficult and demands considerable experience on the part of the analyst. In this connection, therefore, worthy of attention is the use of a selenium photoelement in conjunction with a sensitive galvanometer, as an apparatus which permits more accurate registration of the endpoint.

Gaukhman, Reznik, and Ginsburg [2] who substituted visual observation of the change in color of the indicator by a photoelectric method, used the method of photometric titration for the determination of vanadium and chromium in alloyed steels.

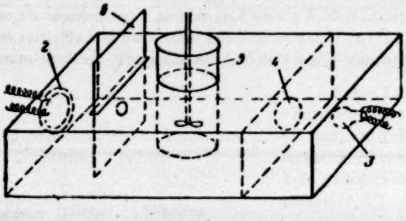

Fig. 1.

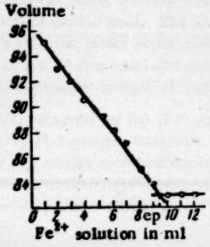

Fig. 2.

Fig. 1. Titration photocolorimeter: 1) Plywood box 24 × 11 × 7 cm; 2) selenium photoelement; 3) 6 volt lamp, 4) condensing lens; 5) cell; 6) diaphragm.

Fig. 2. Titration curve of 10 mg of vanadium with 0.02 N Fe^{2+} solution on the basis of the characteristic color formed; e.p. equivalence point.

Miles and Englis [3] used changes in the characteristic color of quinquevalent vanadium and of dichromate ions, under the action of a reducing agent, for the determination of chromium and vanadium in steels, by a spectrophotometric titration method. The method, according to the authors, gives satisfactory results, but requires preliminary separation of vanadium and chromium.

The present article contains a description of a simple method for the determination of chromium and vanadium in alloys by photometric titration in which a photocolorimeter of simple design is used.

The apparatus is shown schematically in Fig. 1. The light source is a 6 volt automobile lamp fed from an accumulator. The receiver for the light energy is a selenium photoelement. The titration cells are normal 100 ml chemical beakers. Agitation of the solution being titrated is carried out by means of an electrically driven glass stirrer which is kept in the beaker during the whole of the titration. The recording apparatus is a needle galvanometer with a scale divided into 100 divisions, $1^{\circ} = 0.75 \times 10^{-6}$ amps, R = 189 ohm. In order to attenuate the light flow passing through weakly colored solutions, sheets of thick black paper with openings of different diameter are used; the diaphragms are placed in a slit in the upper cover of the apparatus between the cell and the photoelement. The volume of the liquid can be varied within the limits 60 — 80 ml during titration.

TABLE 1

Results of Determination of Vanadium in Ferrovanadium (standard sample 77 a)

As determined by photometric titration, in %	As determined by titration using phenylanthranilic acid as indicator, in %
47.25	47.42
46.04	45.88
46.21	46.10
46.16	45.96

For carrying out a titration, the beaker containing the test solution is placed in the housing of the photocolorimeter, and a diaphragm is chosen so that the galvanometer needle is located towards the end of the scale (90 — 100 divisions); the motor is switched on and the solution titrated with a solution of Mohr's salt; the galvanometer reading (n-divisions) is noted after addition of each aliquot of solution.

The method suggested is based on the reduction of quinquevalent vanadium to the quadrivalent state by Mohr's salt, this reduction being accompanied by the appearance of a blue color. During titration, the galvanometer needle gradually returns to the lower scale divisions, and, after reaching the equivalence point, remains constant.

Typical titration results are shown graphically in Fig. 2. The optimum amount of vanadium in the solution being titrated is 5 — 10 mg. Chromium, nickel, and molybdenum do not interfere with the determination of vanadium under these conditions.

Determination of Vanadium in Ferrovanadium.[*] 0.05 g of ferrovanadium is dissolved on heating in 5 ml of H_2SO_4 (1:3) contained in a 100 ml beaker, and the heating continued for another 1 — 2 minutes. The solution is cooled and diluted with water to 60 — 70 ml, and $KMnO_4$ solution added dropwise until a stable rose color is obtained; excess permanganate is destroyed by addition of a saturated solution of oxalic acid. The beaker is placed in the photocolorimeter and titrated with a 0.02 N solution of Mohr's salt, the latter being added in 2 — 4 ml aliquots initially and then, after addition of about 12 — 14 ml, added in 1.0 ml lots until the galvanometer gives a constant reading. The solution of Mohr's salt is standardized against a standard sample of ferrovanadium.

TABLE 2

Results for the Determination of Vanadium in Steels not Containing Tungsten

Steel, standard sample no.	Certified content of V, in %	Found by photometric titration, in %	Absolute deviation, in %
30	0,26	0,26	±0,00
30v	0,29	0,29	±0,00
		0,28	−0,01
107	0,30	0,32	+0,02
		0,30	±0,00
124a	0,15	0,15	±0,00
		0,16	±0,01

Table 1 contains results obtained for the determination of vanadium in ferrovanadium by photometric titration. For comparison, the Table also contains results obtained during determination of vanadium by visual titration using phenylanthranilic acid as indicator. The time taken for a titration is 5 — 8 minutes.

Determination of Vanadium in Steels not containing Tungsten. To 1.0 — 3.0 g (depending on the vanadium content) of steel is added 30 ml of water and 25 ml of a mixture of acids (15 ml H_2SO_4 sp. gr. 1.84 and 10 ml of H_3PO_4 sp. gr. 1.7). The sample is dissolved initially at room temperature and subsequently on heating. After the sample has dissolved, carbides are destroyed by addition of 0.5 ml of concentrated nitric acid; the procedure subsequently followed is the same as that described for the analysis of ferrovanadium. Results of such vanadium determinations are given in Table 2.

Determination of Vanadium in Steels in the Form of the Phosphotungstovanadium Complex. When tungsten is present in steels, it is possible to carry out photometric titration by making use of the capacity of the phosphotungstovanadium complex to color the solution a dark-violet when the former is reduced by Mohr's salt. During titration of vanadium solutions in the presence of tungsten and phosphoric acid, the light absorption of the solution increases very insignificantly, and only near the equivalence point is there observed a sharp increase in light absorption as the result of the reduction of the phosphotungstovanadium complex; this stage corresponds to displacement of the galvanometer needle towards zero on the scale (Fig. 3). The jump, and also the slope of the straight line,on the graph depend on the vanadium content of the solution. Molybdenum does not affect the position of this jump, since at sulfuric acid concentrations greater than 1.6 N, the phosphomolybdate complex breaks down [4]. Apart from the fact that this phenomenon facilitates the problem of determining vanadium in high-speed steels, it also permits the amount of sample necessary for the analysis of steel not containing tungsten to be reduced. In such cases sodium tungstate is added to the solution prior to titration.

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[*] E. Zimina and I. Iakusheva participated in the experimental work.

1.0 g of steel (for vanadium contents of 0.15 – 0.30%), 0.5 g of steel (for vanadium contents of 0.3 – 1.0%), or 0.2 g (for vanadium contents of 1.0 – 1.9%) is dissolved in 15 ml or 10 ml,respectively,of acid mixture (50 ml water, 50 ml H_2SO_4 sp. gr. 1.84, and 50 ml H_3PO_4 sp. gr. 1.7) on heating. After solution is complete, carbides are destroyed with nitric acid, the solution is then cooled and diluted with water to 60 – 70 ml, and, where the steel does not contain tungsten, 5 ml of a 0.05 N solution of sodium tungstate added (an aliquot of sodium tungstate is dissolved in the minimum amount of 0.5 N sodium hydroxide and the solution acidified to the congo-red endpoint with phosphoric acid; the requisite amount of water is then added); the vanadium is oxidized with permanganate solution and excess of the latter destroyed with oxalic acid. The beaker is placed in the photocolorimeter and titrated with 0.02 or 0.01 N Mohr's salt solution; the latter is added initially in 2 – 3 ml lots, and near the equivalence point in 0.2 – 0.1 ml lots; after 3 – 4 points have been obtained, the Mohr's salt solution is added in 0.5 – 1.0 ml lots until the galvanometer gives a constant reading.

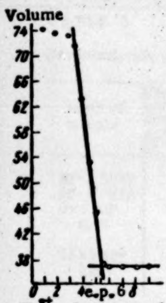

Fig. 3. Titration curve for 3 mg of vanadium with 0.01 N Fe^{2+} solution in the presence of tungsten and phosphoric acid; e.p. – equivalence point.

The results obtained are given in Table 3.

Determination of Vanadium and Chromium in Steels on one Aliquot. The method in which the titration endpoint was determined by means of the phosphotungstovanadium complex was found to be applicable for the determination of chromium and vanadium on one aliquot. In this case, the number of mls of Mohr's salt solution used up for titrating total chromium and vanadium is established first; subsequently, by repeated titration, in the solution oxidized by permanganate solution, the number of mls of Mohr's salt solution used up for reducing vanadium alone is determined. Ammonium persulfate in the presence of a cobalt catalyst [5, 6] is used for oxidizing chromium and vanadium.

TABLE 3

Determination of Vanadium in Steels Using the Phosphotungstovanadium Complex

Steel, standard sample no.	Certified content of V, in %	Found by the photometric titration method, in %	Absolute deviation, in %	Steel, standard sample no.	Certified content, of V, in %	Found by the photometric titration method, in %	Absolute deviation, in %
30	0.26	0.26	± 0.00	122	1.85	1.84	−0.01
		0.28	+ 0.02			1.87	+ 0.02
		0.26	± 0.00			1.89	+ 0.04
30v	0.29	0.29	± 0.00	135	0.29	0.29	± 0.00
		0.30	± 0.01			0.28	−0.01
		0.27	−0.02	156	1.50	1.54	+ 0.04
107	0.30	0,29	−0.01			1.48	−0.02
124a	0.15	0.15	± 0.00			1.49	−0.01
		0.16	−0.01	197	1.26	1.23	−0.03
						1.24	−0.02

TABLE 4

Determination of Chromium and Vanadium in Alloyed Steels

Steel, standard sample no.	Certified content of Cr, in %	Cr, found by photometric titration method, in %	Absolute deviation, in %	Certified content of V, in %	V, found by photometric titration method, in %	Absolute deviation, in %
122	4.17	4.19	+0.02	1.89	1.85	−0.04
156	4.66	4.64	−0.02	1.50	1.56	+0.06
197	4.32	4.24	−0.08	1.26	1.29	+0.03

TABLE 5

Determination of Chromium and Vanadium in Production Samples

Mark of sample	Cr, found by phenyl-anthranilic acid method, in %	Cr, found by photometric titration method, in %	Absolute deviation, in %	V, found by phenyl-anthranilic acid method in %	V, found by photometric titration method, in %	Absolute deviation, in %
RF-1 5879	3.99	3.87	−0.12	1.09	1.04	−0.05
RF-1 6925	4.00	4.00	±0.00	1.08	1.12	+0.04
9×2 MF 6017	1.80	1.71	−0.09	0.18	0.19	+0.01
	1.80	1.76	−0.04	0.18	0.19	+0.01
	1.80	1.81	+0.01	0.18	0.19	+0.01
15×5 MF 6837	5.04	4.98	−0.06	0.13	0.14	+0.01
	5.04	4.96	−0.08	0.13	0.18	+0.05

0.5 g of steel is dissolved in 30 ml of acid mixture (380 ml water, 90 ml H_2SO_4 sp. gr. 1.84, and 60 ml H_3PO_4 sp. gr. 1.7) in a 100 ml beaker. When solution is complete, carbides are destroyed by careful dropwise addition of HNO_3. The solution is evaporated until white fumes of H_2SO_4 appear, hot water is added, followed by 5 ml of 0.05 N tungstate solution (where the steel contains tungsten there is no need to add the tungstate), and 10 ml of the cobalt catalyst (0.5% solution of $CoSO_4 \cdot 7H_2O$) and the whole heated to the boiling point; to the boiling solution is added, carefully, 20 ml of a freshly prepared 25% solution of ammonium persulfate, and boiling continued for 1 – 2 minutes until the raspberry color of permanganate appears; the solution is then kept on a hot plate until the ammonium persulfate has decomposed completely; the solution is boiled again and 10 ml of a 5% solution of NaCl solution added; heating is continued for 5 – 10 minutes after the color of the permanganate has disappeared. The cooled solution is titrated with 0.05 N Mohr's salt solution as described above. When total chromium and vanadium has been titrated, the galvanometer reading becomes constant. Without removing the beaker from the apparatus, the vanadium is oxidized with permanganate, and the vanadium then titrated with 0.05 N Mohr's salt solution.

SUMMARY

A method has been developed for the determination of chromium and vanadium in ferrovanadium and in steels, which is based on photometric titration, and dispenses with the use of an indicator.

The use of the phosphotungstovanadium complex for the determination of chromium and vanadium in high-speed steels excludes the necessity of removing tungsten.

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DETERMINATION OF SULFATES BY REDUCTION TO HYDROGEN SULFIDE

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The most widely used method for the determination of sulfates is their gravimetric determination as $BaSO_4$.

Titrimetric methods of determining sulfates, although they take less time than the gravimetric method, have restricted application, particularly for the determination of small amounts. The most interesting methods of determining sulfates are those based on reduction of sulfates to hydrogen sulfide with a subsequent iodometric finish. Apart from significantly accelerating an analysis, the accuracy of the determination can also be increased when this technique is used.

One of the earliest investigations in this direction was the work of Auger and Gabillon [1], who, for the determination of sulfates, reduced them to hydrogen sulfide by means of hydrogen iodide in the presence of phosphoric acid on heating. Lorant [2] for this purpose used a mixture of hydrogen iodide and formic acid to which a small amount of red phosphorus had been added. Roth [3] used the same medium for the reduction, but instead of red phosphorus suggested potassium hypophosphite as a reducing agent. Hypophosphorous acid was used as reducing agent in a number of subsequent investigations. Thus, Pepkovich [4], Gorak [5], and Archer [6] used a mixture of hydrochloric, hydriodic, and hypophosphorous acids for reducing sulfates.

Rancke-Madsen [7] solved the problem of reducing sulfates in another way, he suggested reducing them by stannous chloride in the presence of phosphoric acid. Since, during the reaction, hydrogen chloride is evolved, which interferes with the absorption of hydrogen sulfide by cadmium acetate solution, Kiba, Takagi, Ioshimura, and Kishi [8] suggested as a reducing agent, a reagent obtained by heating stannous chloride with concentrated phosphoric acid for removal of hydrogen chloride.

This method has been used subsequently for the determination of sulfur in organic materials and for the micro determination of sulfates [9 – 11].

When stannous chloride and phosphoric acid are used for the reduction of sulfates, according to Rancke-Madsen, mercury and copper salts interfere; when the reagent "divalent tin – phosphoric acid" is used, according to the results of Kiba et al, copper and other metals of the same analytical group which give sparingly soluble sulfides interfere.

Taking into account the results obtained in previous work, we made a study of the method of determining sulfates by reducing them to hydrogen sulfide by means of the reagent prepared from divalent tin and phosphoric acid.

The reduction apparatus suggested by Kiba and his co-workers has a number of disadvantages. Concentration of the liquid in it by boiling is very difficult, cleaning of the apparatus takes a long time; in addition, despite the fact that the apparatus is made of quartz, phosphoric acid at 300 deg attacks the walls strongly. We modified the reduction apparatus (Fig. 1).

In order to prevent corrosion of the apparatus walls and for simplifying the preparation of test samples for analysis, we carried out the reaction in a quartz round-bottom beaker – a holder; this, in addition, speeds up the work since changing these holders round takes very little time.

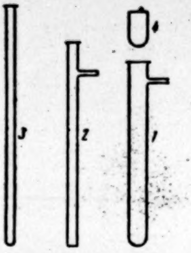

Fig. 1. Details of the reduction apparatus made from transparent quartz: 1) Reaction vessel, about 225 mm long, internal diameter 27 mm; 2) tube for leading in CO_2, about 285 mm long, internal diameter 13 mm; 3) thermometer case, about 340 mm long, internal diameter 8.5 mm; 4) holder, 50 mm long, external diameter 26 mm having a lug on the upper edge, and a mark on the wall corresponding to a volume of 8 ml.

The apparatus (Fig. 2) is assembled by means of rubber stoppers. Flask 6 contains 25 ml of cadmium acetate solution [25 g of $(CH_3COO)_2Cd\cdot2H_2O$ + 1 ml of CH_3COOH per liter) made up to 80 − 90 ml with water. Flask 7 contains 15 ml of the same solution of cadmium acetate made up to 50 − 70 ml with water, and acidified with 2 ml of CH_3COOH. It is essential to make sure that when the apparatus is being assembled, the lower edge of the tube used for leading in the CO_2 is underneath the upper edge of the holder, but not lower than 8 mm above the surface of the reaction mixture.

The apparatus is set up in an asbestos cover for ensuring more uniform heating of the reaction mixture.

CO_2 prepared in the usual way in a Kipps' apparatus is passed successively through cupric sulfate solution, water, and concentrated H_2SO_4, and then through a calcium chloride tower.

According to the directions given by Kiba et al, the reagent used for reducing sulfates is prepared by heating stannous chloride with concentrated phosphoric acid until all the hydrogen chloride has been removed. We found, however, that when these conditions were observed, the reagent obtained did not have a constant activity. Our observations showed that the small amounts of chlorides remaining in the reagent after evaporation, not only did not interfere with the reduction reaction, but, on the contrary, made it go more intensely. Prolonged heating during preparation of the reagent, in order to remove hydrogen chloride, even without taking the temperature above 300 deg, led to an appreciable drop in its reducing capacity, presumably, as the result of the formation of considerable amounts of pyrophosphoric acid.

The reagent used for reducing sulfates is prepared by heating $SnCl_2\cdot2H_2O$ with concentrated phosphoric acid. It is not advisable to use commercial $SnCl_2\cdot2H_2O$ for preparing the reagent, since it may be contaminated with sulfates, and, moreover, may also contain some $SnCl_4$. We recommend that the reagent be prepared as follows: 30 g of metallic tin (analytical grade or chemically pure grade) is treated in a 500 ml quartz flask with excess (200 − 300 ml) hydrochloric acid sp. gr. 1.19. The flask is covered with a small funnel and heated on a water bath until the tin dissolves. When this has been effected, the funnel is removed and the flask placed on an electric hot plate and the liquid evaporated while carbon dioxide is passed through the flask, until a crystalline film is formed. The electric hot plate is then removed and replaced by a vessel containing cold water. When this is done the contents of the flask crystallize almost completely, and only a small amount of sirupy liquid may be left. During evaporation of the $SnCl_2$ solution, 1 − 2 small lumps of tin metal should be added to the flask in order to prevent any possible oxidation.

Concentrated phosphoric acid is prepared by heating 300 g of orthophosphoric acid (analytical or chemically pure grade) sp. gr. 1.7 (approximately 170 ml) in a 500 ml quartz flask using a thermometer in a quartz case; the heating is carried out on an electric hot plate and the vapors liberated are sucked through a tube by means of a water pump. Heating is carried out until the temperature has reached 300 deg, after which the still hot flask is placed in a desiccator and cooled over KOH or $CaCl_2$.

Into a quartz flask containing the $SnCl_2$ prepared beforehand, and heated to the point of incipient fusion in its own water of crystallization, is added the slightly warmed, dehydrated concentrated phosphoric acid, and the mixture agitated and heated on an electric hot plate; the temperature is registered with a thermometer in a quartz case and carbon dioxide is passed over the surface while the liquid is being heated. It is desirable that the heating be carried out rapidly; it should be continued until the temperature reaches 300 deg. Usually, heating takes about 25 − 30 minutes. Hydrogen chloride is thereby removed. The temperature should not be taken beyond 300 deg. If, when the temperature reaches 300 deg, small amounts of HCl continue to come off (test by the appearance of NH_4Cl fumes when a stopper with NH_4OH is brought near the neck of the flask), heating is nevertheless discontinued, since the small amounts of hydrogen chloride which still remain at this stage do not have a deleterious effect on the quality of the reagent obtained, while prolonged heating at 300 does appreciably lower its activity.

The thick sirupy liquid obtained is first cooled in a CO_2 stream (down to 150 deg), and then in a desiccator over KOH or $CaCl_2$ and stored there.

Twice this amount of reagent can be prepared in one lot by doubling the amount of metallic tin and phosphoric acid. During treatment of the $SnCl_2$ with phosphoric acid in this case, heating for removal of hydrogen chloride is continued for a little longer (about 30 — 40 minutes).

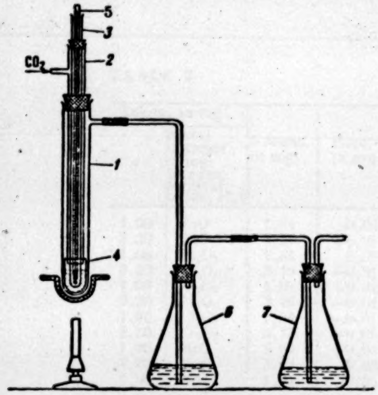

Fig. 2. Apparatus for reducing sulfates: Details 1 — 4 are in Fig. 1; 5) thermometer graduated to 360 deg; 6 and 7) absorption flasks, 200 ml each.

In order to study the reduction of sulfates, an accurately measured amount of standard H_2SO_4 solution was introduced into the quartz holder, and evaporation carried out until the residue is almost dry, reagent is then added, the holder placed in the reduction apparatus and determination carried out as described in the section on "analytical procedure."

As the results given in Table 1 show, fairly consistent results are obtained; the experimental error lies within the limits of a few hundredths of a milligram.

The negative error obtained during determination of large amounts of sulfates, amounting to some tenths of a milligram, depends not so much on incomplete reduction, but on the coating of particles of undecomposed cadmium sulfide by sulfur during the interaction with iodine. This phenomenon is only observed during treatment of large amounts of cadmium sulfide with iodine. During a study of the effect of some of the most common cations, a standard solution of sulfuric acid and a solution of the chloride of one of the metals indicated in Table 2 were measured by means of a pipet into the holder; the holder was then placed on a water bath and the liquid evaporated to dryness. Reagent was then added to the dry residue and the determination carried out as described below.

As the results given in Table 2 show, metals of the second and third analytical groups (Ba, Fe, Al, Cr, Mn, Zn, Co, Ni) do not affect the reduction, and the results obtained are completely satisfactory. Of the elements in the fourth analytical group, Cd, Pb, and Bi do not interfere with the determination. Only bismuth forms a black precipitate of bismuth sulfide during reduction; this precipitate, however, decomposes completely on increasing the temperature further. In the presence of Cu and Hg, the results obtained are very low. In this case the sulfates are also reduced completely, but part of the H_2S formed combines to form the very stable sulfides of copper and mercury which are not completely decomposed under the conditions used for the reaction.

The presence of small amounts of chlorides, of the order of 0.1 g in the test sample, favors a more intensive reduction reaction. The amount of cadmium acetate in the receiver ensures a sufficient buffering capacity to suppress the effect of hydrogen chloride driven into the receiver on the deposition of cadmium sulfide. The presence of too large amounts of chlorides may give rise to such conditions that, as a result of increased acidity in the first absorption flask, the liberated hydrogen sulfide will not be bound by the cadmium and will break through into the second flask, and thus give rise to partial losses. Accordingly, when large amounts of chlorides are present, it is essential to remove some of them by evaporation on a sand bath with a few drops of dehydrated phosphoric acid at 140 — 150 deg.

As was to be expected, even insignificant amounts of nitrates interfered; they must be removed by repeated evaporation with hydrochloric acid on a water bath.

Results for the determination of sulfates in natural materials (natural gypsum and Black Sea slime) are given in Table 3.

TABLE 1

S taken, in mg	S found, in mg	Error, in mg	S taken, in mg	S found, in mg	Error, in mg
11,20	11,11	−0,09	0,80	0,81	+0,01
11,20	11,08	−0,12	0,80	0,78	−0.02
8,00	7,92	−0,08	0,32	0,34	+0,02
8,00	7,95	−0,05	0,32	0,31	−0.01
4,00	4,00	±0,00	0,16	0,17	+0,01
4,00	3,99	−0,01	0,16	0,16	±0,00
1,60	1,63	+0,03	0,08	0,08	±0,00
1,60	1,59	−0,01	0,08	0,09	+0,01

TABLE 2

Taken, in mg		S found, in mg	Error, in mg	Taken, in mg		S found, in mg	Error, in mg
S	Metal chloride, calculated in terms of oxide, 10.0			S	Metal chloride, calculated in terms of oxide, 10.0		
1,60	BaO	1,64	+0,04	3,20	NiO	3,19	−0,01
3,20	BaO	3,21	+0,01	1,60	CoO	1,61	+0.01
1,60	Fe_2O_3	1,54	0,06	3,20	CoO	3,14	−0,06
3,20	Fe_2O_3	3,19	−0,01	1,60	ZnO	1,65	+0,05
1,60	Al_2O_3	1,62	+0.02	3,20	ZnO	3,17	−0,03
3,20	Al_2O_3	3,16	−0,04	1,60	CdO	1,59	−0.01
1,60	Cr_2O_3	1,59	−0,01	3,20	CdO	3,17	−0,03
3,20	Cr_2O_3	3,15	−0,05	1,60	PbO	1.57	−0,03
1,60	MnO	1,64	+0,04	3,20	PbO	3,18	−0,02
3,20	MnO	3.18	−0,02	1,60	Bi_2O_3	1,65	+0,05
1,60	NiO	1,64	+0,04	3,20	Bi_2O_3	3,16	−0,04

In addition, sulfates were determined in sea-water. Using the classical gravimetric method, 0.00233 g of S was found in 5 ml of sea-water. Using the same volume of sea-water, and evaporating to dryness on a water bath, 0.00237 g of S was found by determination by the method involving reduction to H_2S.

Experimental Procedure. The most convenient amount of sample to take for analysis is that which contains about 0.5 − 5 mg of sulfate sulfur (calculated on the basis of S).

When the test material is a dry material, an aliquot of it is placed in the quartz holder and moistened with 2 − 3 ml of a 2% solution of potassium chloride and the mixture evaporated to dryness on a water bath.

When a solution is being analyzed, it is placed in a holder and potassium chloride added, when necessary, in the amount just quoted, and the whole evaporated to dryness.

When the test material contains nitrates, the dry residue in the holder is treated with concentrated hydrochloric acid and the mixture evaporated to dryness; this operation is repeated three times.

When very large amounts of chlorides are involved (more than 0.2 g), it is recommended that 3 − 4 drops of concentrated phosphoric acid be added to the dry residue, and the whole heated on a sand bath at 140 − 150 deg for 30 − 40 minutes for removing the bulk of the chlorides.

To test material prepared in any of the ways indicated, and contained in a holder is added 8 ml of reagent (to the mark on the holder), and, using a wire with a hook on it, the holder is transferred into the apparatus. The apparatus is sealed with a stopper filled with a tube for leading in CO_2, and with a thermometer. The absorption apparatus containing cadmium acetate is then connected and CO_2 passed for 3 − 5 minutes in order to drive the air from the apparatus. The apparatus is then heated over a small gas burner flame at such a rate that a temperature of 300 deg is reached in 15 − 20 minutes.

TABLE 3

Sample	S found, in %	
	By a gravimetric method	By reduction to H_2S
Gypsum	18.82	18.81
Grey slime	0,100	0,102
Black slime	0,066	0,067

Reduction starts at a temperature as low as 120 – 150 deg for high sulfate contents, the liquid in the holder becomes turbid as a result of deposition of elemental sulfur, the latter obviously being the intermediate form during reduction; on heating further, the sulfur is reduced to hydrogen sulfide and the liquid in the holder becomes clear.

At approximately 240 – 250 deg the reduction process starts to proceed vigorously as is evident from the bubbles of hydrogen sulfide liberated. When the temperature reaches 300 deg it is kept there for a further 25 – 30 minutes in order to complete the reduction. In order to check that reduction has gone to completion, the absorption tube can be disconnected and the gas issuing from it tested for hydrogen sulfide by means of lead acetate paper, or by its smell. When reduction is complete, the receiver containing cadmium sulfide is removed, and, using a piece of ashless filter paper, the sulfide adhering to the end of the tube wiped off; the contents of the receiver and the filter paper are shaken together and the whole added to acidified 0.02 N iodine solution. The flask is stoppered and then allowed to stand for 20 – 30 minutes, the contents being periodically shaken during this time; finally, excess iodine is titrated with 0.02 N thiosulfate.

1 ml of 0.02 N iodine corresponds to 0.00032 g S. For determining amounts of sulfur less than 0.5 mg, it is best to use 0.01 N iodine and thiosulfate.

SUMMARY

1. A study has been made of a method for determining sulfates by reducing them to hydrogen sulfide by means of a reagent prepared by evaporating divalent tin with concentrated orthophosphoric acid. Optimum conditions for preparing the reagent have been established.

2. A modified apparatus is described for carrying out the determination; rapid charging and prevention of corrosion of the apparatus by phosphoric acid are special features of the apparatus.

3. The method has been tried out on pure salts; it has been confirmed that calcium, barium, iron, aluminum, chromium, manganese, cobalt, nickel, and zinc do not interfere with sulfate determination. It has been established that the presence of the alkali metal chlorides in amounts up to 0.2 g accelerates the reduction process.

4. It has been established that bismuth, lead, and cadmium do not interfere with the reduction. It has been confirmed that copper and mercury salts interfere.

5. The method has been tried out on natural materials such as: gypsum, Black Sea silt, and sea water.

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POLAROGRAPHIC DETERMINATIONS OF IODIDES IN MOLTEN SALTS

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Previous articles have dealt with the possibility of determining various anions in the anodic and cathodic regions in a supporting electrolyte consisting of molten nitrates (KNO_3 + $NaNO_3$) using the electrodes Pt_{micro} — Pt_{macro} [1]. It was established that a number of anions give stable waves in the cathodic and anodic regions. The behavior of chromates and nitrites in a supporting electrolyte of molten nitrates [2, 3] was studied in greater detail. The object of our further research was the I^- ion which gives well-defined waves in the anodic region.

The setup and the technique used have been described before [1 — 3].

Within the temperature range 270 — 390 deg, I^- ions give two well-defined waves on the polarograms in the anodic region. The first of these waves (the oxidation potential of which with respect to the platinum cathode is +0.8 — +0.6 volt) corresponds to anodic oxidation of iodide ions. The wave height depends on the concentration of iodide introduced; when the oxidation potential is reached, liberation of violet bubbles of gas on the electrode is observed for all temperatures. The second wave, which is absent in the supporting electrolyte of nitrates, and only appears when iodide is added to the melt, corresponds to the wave for NO_2^- ions is confirmed by the nearness of the oxidation potentials and half-wave of pure nitrite, and the second wave obtained. When the melt is acidified by addition of $KHSO_4$, the second wave disappears, while the first wave remains unaltered. The addition of an aliquot of $NaNO_2$ to the iodide melt increases the height of the second wave. Formation of NO_2^- in the melt after addition of KI can be explained by the occurrence of the reaction $2KI + KNO_3 \rightleftarrows I_2 + KNO_2 + K_2O$. Potentiometric studies confirmed that this reaction does in fact occur.

TABLE 1

Reproducibility of Iodide Waves With Time

Temperature, in °C	Weight of KI, in mg	Wave height, in mm on the scale				
		Immediately	After 15 min.	After 30 min.	After 60 min.	After 120 min.
200±5	150,0	7,0	7.5	8.0		
		8,0	7,5	8,0		
		7,0	9.5	10.0	8,0	8,0
345±5	100,0	17,0	14.0	15.5	14.0	13.0
			16,0	18.0	14.5	14,5
			15.5	14,5	14.5	13,5
385±5	50,0	5,5	4,0	5,5	5,5	
		3,5	3,0	3,0	3,5	

Despite the interaction which occurs between KI and KNO_3, determination of I^- in a melt by a polarographic method is fully possible, as shown below. Obviously, some equilibrium state is established in the molten salts, and the iodide content can be determined polarographically.

The height of the first wave for I^- does not change during 30 — 120 minutes after addition of the aliquot of iodide, and exhibits fairly good reproducibility, as can be seen from the results given in Table 1.

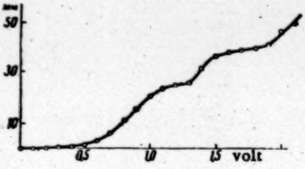

Fig. 1. Polarogram for the iodide ion.

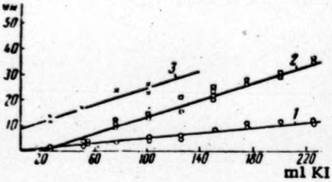

Fig. 2. Calibration curves for KI:
1) 280°; 2) 350°; 3) 390°.

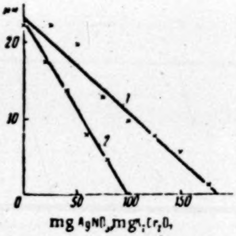

Fig. 3. Curve for amperometric titration:
1) 200 mg of KI with micro amounts of $AgNO_3$; 2) 200 mg of KI with micro amounts of $K_2Cr_2O_7$ at 280°.

The forward and reverse courses of the polarographic waves do not coincide. This is connected with changes which occur on the electrode during the polarographic process, particularly at elevated temperatures; these changes are manifested as blackening of the anode surface. In order to get reproducible results, it is necessary to clean the electrodes by calcining them.

During the determination of the half-wave potential with respect to the indifferent glass electrode, the graph for $E \log \frac{i}{i_d - i}$ proved to be a straight line. At 340 ± 5 deg, the half-wave potential is $E_{\frac{1}{2}} = 0.32 \pm 0.02$ volt, and is almost independent of the iodide concentrations.

In order to establish the behavior of the electrodes during the polarographic process, a study was made of changes in the electrode potentials during the polarographic process, with respect to a glass reference electrode, which was described in a previous article [3]. It was found that during the initial stages of the appearance of the polarographic wave, the anode potential changes only insignificantly while that of the cathode changes sharply. When the limiting current is reached, the anode potential changes sharply, while the cathode potential hardly changes at all.

In order to characterize the behavior of iodide ions, the temperature coefficient of the diffusion current was determined by two methods describe previously [3]. The temperature coefficient had a value of 1.5%/degree.

There is a linear relation between the value of the diffusion current and the iodide concentration of the melt (Fig. 2). Determination of various amounts of KI by means of a calibration curve gives completely satisfactory results (Table 2).

We were interested in the possibility of carrying out an amperometric titration of iodide ions in molten salts.

During titration of I^- with micro amounts of $AgNO_3$, a yellow insoluble precipitate of AgI is formed in the melt, and the height of the iodide wave gradually decreases. As can be seen from Fig. 3, the equivalence point, according to the amperometric curve, is fairly clear-cut. Titration gives satisfactory results (Table 3).

A systematic error on the side of low results for the amount of KI is always observed. This can be explained on the grounds that some of the KI, as mentioned already, reacts with the NO_3^- ions.

Titration of iodide ions with the oxidizing agent $K_2Cr_2O_7$ was carried out in both neutral and acid media. On addition of micro amounts of the oxidizing agent to a melt containing KI, the wave height for I^- gradually increases, giving a well-defined curve during amperometric titration (Fig. 3). Determination of the equivalence point is also fairly easy. Titration results are given in Table 4.

If it is assumed that the reaction $K_2Cr_2O_7 + 6KI \rightarrow 3I_2 + 2KCrO_2 + 3K_2O$, for which the molar ratio $K_2Cr_2O_7$/KI is equal to 0.166, takes place in the melt, then, as can be seen from Table 4, the amount of $K_2Cr_2O_7$ used up for titration is considerably greater. During potentiometric titration of dichromate with potassium iodide in a melt at the same temperatures, there is observed an increased expenditure of dichromate.

In Fig. 4 is shown the curve obtained during the potentiometric titration of 50 mg of $K_2Cr_2O_7$ with micro aliquots of KI in a neutral melt. As is evident from this Fig., the equivalence point lies at 96 mg, which corresponds to a ratio of $K_2Cr_2O_7/KI = 0.3$, which is close to the value found polarographically. The molar ratio found corresponds more closely to the reaction $4K_2Cr_2O_7 + 12KI \rightarrow 8KCrO_2 + 12KIO \rightarrow 8KCrO_2 + 6K_2O + 6I_2 + 3O_2$. That this reaction does in fact occur should be proved by additional experiments or by other methods of investigation.

In one of the previous investigations on the polargraphy of cations in a supporting electrolyte of fused nitrates [4], the process of complex formation between cadmium and iodide ions was detected polarographically. The existence of this reaction was also confirmed in the present investigation, and an attempt was made to use it for amperometric titration of iodide ions in the melt.

On addition to a molten salt (temperature 290°), containing iodide atoms, of micro aliquots of cadmium nitrate, the iodide wave disappeared and a new wave appeared at a more negative potential, namely at 0.3 − 0.4 volt relative to the platinum cathode. The addition of cadmium iodide instead of potassium iodide gave a wave at a potential of 0.3 − 0.4 volt. The height of this wave is proportional to CdI_2 concentration, but its height is approximately half of that of the wave obtained for an equimolecular concentration of $K_2[CdI_4]$. Obviously complex formation of $2CdI_2 \rightarrow Cd[CdI_4]$ occurs in the melt.

TABLE 2

Determination of KI in a Molten Salt

Temperature, in °C	KI taken, in mg	KI found, in mg	Error, in %
280	116	114	−2
	200	180	−10
350	75	85	+13
	100	94	−6
380	25	29	+16
	100	80	−20

Mean experimental error ± 11%

TABLE 3

KI taken, in mg	$AgNO_3$ used, in mg	KI found, in mg	Error, in %
200	195	190.4	−5
176	180	170.0	−4
81	82	80.0	1.3

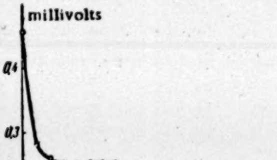

Fig. 4. Potentiometric titration curve for 50 mg of $K_2Cr_2O_7$ with micro amounts of KI.

TABLE 4

Titration of KI with Micro Amounts of $K_2Cr_2O_7$

Temperature, in °C	Medium	Ki taken, in moles	$K_2Cr_2O_7$ used, in moles	Molar ratio $/K_2Cr_2O_7/$ $/KI/$
280	Neutral	$1{,}2 \cdot 10^{-3}$	$0{,}34 \cdot 10^{-3}$	0,28
	»	$1{,}2 \cdot 10^{-3}$	$0{,}30 \cdot 10^{-3}$	0,25
	Acid	$1{,}2 \cdot 10^{-3}$	$0{,}54 \cdot 10^{-3}$	0,45
	»	$1{,}2 \cdot 10^{-3}$	$0{,}37 \cdot 10^{-3}$	0,41
350	Neutral	$1{,}2 \cdot 10^{-3}$	$0{,}29 \cdot 10^{-3}$	0,24
	»	$1{,}2 \cdot 10^{-3}$	$0{,}36 \cdot 10^{-3}$	0,30
	»	$0{,}9 \cdot 10^{-3}$	$0{,}32 \cdot 10^{-3}$	0,36

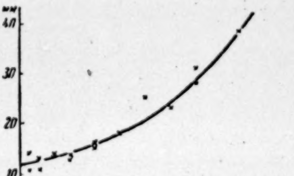

Fig. 5. Calibration curve for NaI.

In order to make sure that the waves indicated do in fact belong to the complex $[CdI_4]^{2-}$, the complex $K_2[CdI_4]$ was synthesized in the solid state and added to a melt. The same clearly defined wave was again detected on the polarogram at 0.3 volt. There was found to be a linear relation between the concentration of the complex and the wave height.

The analogous iodide complex of lead is apparently unstable. Attempts to use the process of complex formation for determination of iodide ions in melts did not give good results.

We thought it would be of interest to clarify the behavior of iodide ions in a supporting electrolyte of fused chlorides. The supporting electrolyte tried was a mixture of equal parts of potassium, sodium, and lithium chlorides. The work was carried out at a temperature of 700 – 750 deg. On addition of sodium iodide to the fused chlorides, fairly clearly defined waves were obtained in the anodic region, almost from zero applied potential. The relation between wave height and concentration of sodium iodide is a complex one (Fig. 5).

N. Zotova and E. Levinzon, who are students at the Kishinev University, took part in the work described here.

SUMMARY

It has been shown that it is possible to determine I^- polarographically in a supporting electrolyte of fused nitrates at temperatures of 270 – 390 deg, and in fused chlorides at temperatures of 700 – 750 deg. It has been established that there is a linear relation between the concentration of iodide ions in the melts and the height of the polarographic wave when fused nitrates are used as the supporting electrolyte. The half-wave potentials of I^- in fused nitrates have been determined. It has been shown that it is possible to carry out amperometric titration of I^- with micro aliquots of silver nitrate and potassium dichromate.

The occurrence of complex formation between I^-, Cd^{2+}, and Pb^{2+} in fused nitrates has been confirmed.

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RAPID METHODS OF MICROELEMENTAL ANALYSIS

COMMUNICATION 15. THE SIMULTANEOUS MICRO DETERMINATION OF CARBON, HYDROGEN, AND HALOGENS IN ORGANIC COMPOUNDS*

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In previous articles we have described methods for the simultaneous micro determination of carbon, hydrogen, and halogens by pyrolytic combustion in an empty tube [1 – 2], and also described apparatus which we have innovated [3]; in addition, the characteristics of the elemental analysis of halogen-containing materials have been considered [4]. It was established that the presence of halogens, or of halogen-containing materials, exhibits an inhibiting action on the oxidation of carbon to carbon dioxide, as a result of which, the gases issuing from the combustion tube have been found to contain carbon monoxide. In order to ensure quantitative oxidation of carbon to CO_2 during the analysis of halogen-containing compounds, it was found necessary to introduce platinum contacts into the oxidizing zone. At the same time it was shown that, in those cases where absorption of the halogen was carried out immediately after the products of pyrolytic combustion had left the quartz test tube, and the gases freed from halogen passed into the oxidizing zone, quantitative conversion of carbon into CO_2 could be achieved without using a platinum catalyst. Nevertheless, as pointed out already [4], such an experimental technique would preclude simultaneous determination of C, H, and halogen.

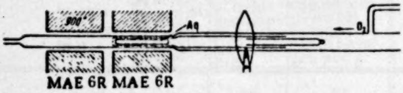

Fig. 1. Apparatus for the simultaneous determination of carbon, hydrogen, and halogens.

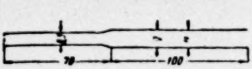

Fig. 2. "Case" 8.5 and 11 mm external diameter; 9 mm internal diameter.

Recently a technique has been developed in our laboratory, in which, by carrying out the combustion in a so called "case" [5], it has been found possible to introduce essential improvements into the determination of carbon, hydrogen, and halogens. In this new variant, the tube containing the sample, silver, and the oxidizing zone are arranged successively in the gas flow in the combustion tube. For this purpose the silver and the tube containing the sample are placed in a hollow thin-walled quartz "case" (Fig. 2), which, after combustion, is removed from the tube and weighed. In this case, as mentioned already [4], there is no need to place platinum contacts in the oxidizing zone, but, at the same time it is possible to weigh the silver by using the "case". The weight of the "case" is almost half that of the apparatus used previously, which included a heavy ground joint; accordingly, it is possible to achieve considerably better reproducibility in weighing the silver, and, thereby, essentially improve the accuracy of halogen determination. In addition, there is no further need to use a combustion tube with ground joints, and the life of the tube itself is increased (Fig. 3), since it is not corroded by the silver which is located in the "case".

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* For Communication 14, see J. Anal. Chem. 12, 526 (1957).

The halogens are absorbed by pure metallic silver in the form of foil, mesh, or wire,* or by silver precipitated on a carrier. When metallic silver is used in the "case" about 1.5 g is introduced into the "case"; this is approximately half the amount used in the ground-joint absorption apparatus [4]. The layer of silver 5 – 6 cm long is heated with the MAG-6R electric oven to 550 – 600 deg. This amount of silver can be used for 30 – 40 determinations; this corresponds to an increase in weight as a result of absorption of halogen of about 70 mg. Table 1 contains results for the absorptive capacity of metallic silver expressed in milligrams of halogen per g of silver. Comparison of our results with those of Mitsui [6], which he obtained during a detailed study of the determination of halogens in organic compounds, confirm a conclusion which we had already come to previously, that the absorptive capacity of metallic silver depends not only on its surface area, but also on the temperature [4]. In the case under discussion, increasing the temperature from 425 – 575 deg led to the absorptive capacity increasing several times.

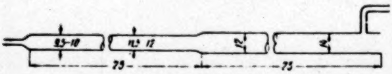

Fig. 3. Combustion tube. 9.5 – 10 mm and 12 mm internal diameter; 11.5 – 12 mm and 14 mm external diameter.

Our experiments also confirmed results obtained by Mitsui which showed that silver preparations with a large surface area have a good absorptive capacity at temperatures which are too low for use with silver mesh or foil. Of particular interest in this connection is a preparation of silvered pumice, since, according to our observations, silver deposited on a porous carrier absorbs halogen very well, and corrodes the walls of the quartz tube to a considerably lesser extent than metallic silver. This is a consequence of the fact that the main bulk of the silver halide is held by the well-developed surface and does not fall on the quartz walls. For the simultaneous determination of C, H, and halogen, we tried granulated, silvered pumice prepared according to Sokolova's method [7], and became convinced of its completely suitability for our purpose. The silvered pumice was tested at 425 deg, i.e. at a temperature which is lower than the melting point of the silver halide, which is 455, 434, and 588 deg for AgCl, AgBr, and AgI, respectively. In the course of these tests it established that the absorptive capacity of this preparation was almost double that of the electrolytic silver proposed by Mitsui (Table 2).

TABLE 1

Absorptive Capacity of Metallic Silver at 575 deg

Weight of silver, in g	Number of determinations carried out with same aliquot of silver	Amount of halogen trapped by the silver in mg	Absorptive capacity of silver for halogen, in mg of halogen per g	Weight of silver, in g	Number of determinations carried out with same aliquot of silver	Amount of halogen trapped by the silver in mg	Absorptive capacity of silver for halogen, in mg of halogen per g
1,45	42	88	61	1,36	40	81	60
1,18	32	77	65	1,62	32	65	40
1,18	25	76	64				
0,80	18	47	59	Mean 1,27		72	58

In addition to more complete use of the silver, another advantage of working with such a preparation is that, thanks to absorption of the halogen at a comparatively low temperature (425 – 575 deg), corrosion of the case is so insignificant, that the latter can be used repeatedly with fresh lots of preparation.

When metallic silver is used, the silver halide spills over the "case", which, as a rule, comes out of the stream after the first series of experiments.

The silvered pumice should not completely fill the cross section of the "case", since, if this is done, there will be some resistance to the gas flow, which will be sufficient to direct part of the gaseous combustion products into bypassing the pumice layer.

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* We had at our disposal silver foil 0,04 mm thick, and mesh made from 0,1 mm diameter wire.

TABLE 2

Absorptive Capacity of Various Silver Preparations

	Metallic silver in the form of mesh, foil, or wire		Electrolytic silver	Silvered pumice
	Mitsui's results	Author's results	Mitsui's results	Author's results
Temperature at which the silver is heated	425°	575°	425°	425°
Absorptive capacity expressed in mg halogen per g of silver	3.7	55	162	292

TABLE 3

Determination of Carbon and Chlorine in Hexachloroethane

Test material	C, in %		Cl, in %		Total C and Cl, in %	Notes
	found	difference	found	difference		
Hexachloroethane	7.68	−2.46	82 85	−6.99	90,53	Combustion carried out with a gas burner
C_2Cl_6	9.59	−0,55	85.72	−4.14	95,31	
C—10.14%	10.25	+0,11	89.66	−0.20	99.91	Combustion carried out with an electric oven
Cl—89.86%	10,22	+0,08	89,59	−0,27	99,81	

Experimental Procedure. Before commencing an analysis, a blank is carried out while the ovens are on. For this purpose, the "case" containing the silver is moved into the combustion tube, and the oven fitted onto the part where the silver is located; when metallic silver is used,the oven temperature is raised to 575 deg. while when silvered pumice is used the temperature is adjusted to 425 deg. The absorption apparatus is connected to the combustion tube and 500 ml of oxygen passed through at a rate of 35 − 40 ml/minute. When the blank test is finished,the absorption apparatus is disconnected, and, after wiping it and removing the electric charge on it, it is transferred to the balance. The electric oven is removed from the "case" and the latter is then cooled in a weak oxygen stream in the course of 7 − 8 minutes. The "case" is removed from the combustion tube by means of a hook, and is then electrically discharged by passing it over the oxidizing flame of a burner, and placed on a long block near the balance. The absorption apparatus is weighed 15 and 20 minutes after wiping. After weighing the absorption apparatus, the "case" is weighed 25 minutes after wiping the apparatus. The weighed apparatus is connected to the setup and left under oxygen pressure with the aspirator tap closed. An aliquot of test material is weighed into a tube and the latter placed in the "case", the whole is then placed in the combustion tube. The tube containing the sample is placed approximately halfway along the "case". In some cases the analyst may find it more convenient to use a tube 9 cm long; the latter is placed at a position $\frac{1}{3}$ the length of the "case". Long tubes are used for pyrolysis of readily volatile compounds (b.p. 40 − 50 deg) and organosilicon compounds which contain halogens. Combustion of fully halogenated hydrocarbons is best carried out with a MAG-6R electric oven at 900 deg rather than with a gas burner. Table 3 contains some comparative results which show that analysis of hexachloroethane by means of a gas burner leads to incomplete combustion. Results of analysis of halogen-containing materials carried out by the technique just described are given in Table 4.

The same operational procedure and apparatus can also be used for the simultaneous determination of C, H, and S, the only difference in this case is that the silvered pumice is kept at a temperature of 750 deg. It is

TABLE 4

Simultaneous Determination of Carbon, Hydrogen, and Halogen

Test material	Amount of sample taken, in mg	C, in %		H, in %		Halogen, in %	
		found	difference	found	difference	found	difference
1, 1, 1,2-Tetrachloro-3-p-tolylpropane	6,558	44,16	+0.01	3,78	+0,07	52,20	+0,06
$C_{10}H_{10}Cl_4$	6,884	44,14	−0,01	3,80	20,09	52,22	+0,08
C—44, 15%; H-3,71%; Cl-52, 14%							
Hexachloroethane	8.145	10,22	+0,08	—	—	89,53	−0,33
C_2Cl_6	9,900	10.30	+0,16	—	—	89,71	−0,15
C—10, 14%; Cl−89, 86%							
p-Chlorosuccinic acid	7,444	59.13	−0,06	3.78	−0.08	19 21	−0,21
$C_6H_7ClO_2$	9,767	59,09	−0,10	3,94	+0,08	19,25	−0,17
C—59, 19%; H—3, 86%; Cl—19, 42%							
Bromobenzoic acid	6,015	42.01	+0,19	2.61	+0.10	39.87	+0,12
$C_7H_5BrO_2$	6,860	41,95	+0.13	2,66	+0.15	39,61	−0,14
C—41, 82%; H—2, 51%; Br-39, 75%							
α, β-Dibromoethyl-2-propoxybenzene	8,387	41.28	+0,17	4.50	+0,12	49,74	+0,11
$C_{11}H_{14}Br_2O$	6,112	41,10	+0,09	4,49	+0,11	49,49	−0,14
C—41, 01%; H—4, 38%; Br-49, 63%							
Acetovinyltrimethyl-ammonium chloride	6,615	51,27	−0,10	8,64	+0,02	21.87	+0,20
$C_7H_{14}ClNO$	8,050	51,30	−0.07	8,66	+0,04	21,64	−0,03
C—51, 37%: H—8, 62%; Cl − 21, 67%							
Triphenyloxonium iodide	6,960	57,91	+0,14	4,03	−0,01	34.31	+0,39
$C_{18}H_{15}IO$	7,778	57,99	+0,22	4.03	−0,01	34.07	+0,15
C—57, 77%; H—4, 04%; I—33, 92%							
2-Phenyldihydroquinolizine perchlorate	6,526	59.00	+0,07	4.04	+0,08	11,55	−0,05
$C_{15}H_{12}ClNO_4$	6,410	59,07	+0,14	4.07	+0,11	11,73	+0 13
C-58, 93%; H—3,96%; Cl—11, 60%							

necessary to use different "cases" for the determination of sulfur and halogens. Results for the determination of C, H, and S are given in Table 5.

As is evident from the results given in Tables 5, 6, and 7, in those cases where the test material contains halogen or sulfur, the technique involving the use of a "case" is applicable to methods developed earlier for the simultaneous determination of several elements on one aliquot of test material, namely, to the determination of carbon, hydrogen, halogen, and silicon [8 − 11], carbon, hydrogen, sulfur, and phosphorus [12 − 14], carbon, hydrogen, halogen, or sulfur and metal [4]; the latter is possible only when, as the result of combustion, nonvolatile metal oxides or salts which are stable at a temperature of 900 deg are obtained. Determinations which we have carried out of carbon, hydrogen, halogen, and inorganic residue on one aliquot of test material which contained in addition to C, H, and I, one atom each of phosphorus and copper, showed that under the conditions of pyrolytic combustion, the weight of inorganic residue corresponds to copper pyrophosphate, and that it is possible on the basis of this residue to calculate the content of copper and phosphorus in materials of a similar type (Table 7). The results given in Tables 4, 5, 6, and 7 illustrate the possibilities which are opened up by the use of pyrolytic combustion during the analysis of organic compounds with a complex composition.

TABLE 5

Simultaneous Determination of Carbon, Hydrogen, Sulfur, and Some Other Elements

Test material	Amount of sample taken, in mg	C, in %		H, in %		S, in %		P, in %		Fe,* in %	
		found	difference	found	difference	found	difference	found	difference	found	difference
Sulfanilic acid	8.741	41,84	+0,23	4,21	+0.14	18.51	−0				
$C_6H_7NO_3S$ C−41,61%; H−4,07%; S−18,51%	7,700	41,61	0	4,22	+0.15	18,47	−0,04				
Phenylsemicarbazone of 0,0-diethyl-S-acetonyldithiophosphate	6,790	58.25	−0,10	8,02	−0,14	8,65	0				
$C_{18}H_{30}N_2O_4S$ C−58,35%; H−8,16%; S−8,65%	5,848	58,29	−0,06	8,01	−0,15	8,69	+0,04				
Phenylsemicarbazone of 0,0-diethyl-S-acetonyldithiophosphate	5,578	44,82	+0,04	5,73	−0,18	17,14	+0,06	8,19	−0,06		
$C_{14}H_{22}N_3O_3PS_2$ C−44,78%; H - 5,91%; S−17,08%; P−8,25%	5,761	45,00	+0,22	6,01	+0,10	17,06	−0,02	8,19	−0,06		
Ferrocenylthiocyanomethane	7.045	55.95	−0,10	4,32	+0 01	12.18	−0,29	—	—	21,88	+0.16
$C_{12}H_{11}FeNS$ C−56,05%; H - 4.31%; S−12,47%; Fe−21,72%	5,682	55,87	−0,18	4,45	+0,14	12,02	−0,45	—	—	21,54	−0,18

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* Calculated from the weight of Fe_2O_3

TABLE 6

Simultaneous Determination of Carbon, Hydrogen, Chlorine, and Silicon

Test material	Amount of sample taken, in mg	C, in %		H, in %		Cl, in %		Si, in %	
		found	difference	found	difference	found	difference	found	difference
Methyldodecyldichlorosilane $C_{13}H_{28}Cl_2Si$ C–55,11%; H–9,96%; Cl–25.03%; Si–9, 90%	5 890 5,670	55,32 55,28	+0.21 +0,17	9,93 9,90	+0,03 –0,06	24,70 25,22	–0.33 +0,19	9,57 9,80	–0.33 –0,10
Decyltrichlorosilane $C_{10}H_{21}Cl_3Si$ C–43,56%; H–7,68%; Cl–38,58%; Si–10,18%	7.725 5,802	43.68 43,71	+0.12 +0,15	7,79 7,71	+0.11 +0,03	38.21 38,03	–0,37 –0,55	10,58 10,55	+0,40 +0,37

TABLE 7

Simultaneous Determination of Carbon, Hydrogen, Iodide, and Inorganic Residue

Test material	Amount of sample taken, in mg	C, in %		H, in %		I, in %		Cu, in %		P, in %*	
		found	difference	found	difference	found	difference	found	difference	found	difference
Complex formed between copper iodide and dipropyl phosphinate $C_{12}H_{19}CuIO_2P$ C–34,59%; H–4,60%; I–30,46%; Cu–15,25%; P–7.44%;	7,718 7.296	34,47 34,58	–0,12 –0,01	4,65 4,73	+0,05 +0.13	30,77 30,25	+0,31 –0,21	15 35 15,36	+0,10 +0,11	7,49 7,49	+0,05 +0,05
Complex formed between copper iodide and diethyl phenylphosphinate $C_{10}H_{15}CuIO_2P$ C–30,90%; H–3,89%; I–32,66%; Cu–16,35% P–7,97%	7,720 6,130	30,81 30,55	–0,09 –0,35	3,91 3,83	+0,02 –0,06	33,08 33,25	+0,42 +0,59	16,35 16,18	— –0,17	7,97 7,89	— –0,08

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* Calculated on the basis of a residue of $Cu_2P_2O_7$.

SUMMARY

An improved modification of the method for the simultaneous determination of C, H, and halogen has been developed. Thanks to the use of a "case", the accuracy of determination of the halogen is high, and there is no need to use platinum contacts, while a combustion tube of the normal type without any ground-glass joints can be used.

Silvered pumice is used for absorbing the halogens, and it has been demonstrated that this material can be used at 425 deg; it has been shown that at this temperature the absorptive capacity of silver precipitated on pumice is considerably greater than that of electrolytic silver.

The method described is also applicable to the determination of C, H, and S, and for the determination of several elements on one aliquot of test material, in accordance with methods developed previously.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF HALOGENS IN ORGANIC MATERIALS

COMMUNICATION 3. SIMULTANEOUS, INDEPENDENT, GRAVIMETRIC DETERMINATION OF CHLORINE, BROMINE, AND IODINE TAKEN TWO AND THREE ELEMENTS AT A TIME*

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In our first two communications we described new methods for the quantitative determination of chlorine, bromine, and iodine in organic materials [1]. The present article is devoted to the quantitative determination of the halogens, taken two and three elements at a time, on one aliquot of test material. Some of the methods for the simultaneous quantitative determination of halogens are long and complicated to carry out [2]. The principle of our method is based on displacement of the less active halogens from potassium and sodium bromides and from potassium iodide by the more active halogens.

At room temperature, the reaction of mutual liberation which occurs between the halogens does not occur in the absence of water. As we found out, on raising the temperature, the capacity of the halogens to liberate one another from their compounds with metals rapidly increases; the reaction is quantitative at temperatures of 680 – 720 deg for sodium and potassium bromides, and at 480 – 520 deg for potassium iodide.

The temperature should not be taken over those indicated above, since, in the case of the bromides, they fuse, while the iodides start to decompose appreciably.

The apparatus is assembled as shown in the diagram.

The first oven is heated to 750 – 800° deg, the second to 800 – 900° deg, the third to 680 – 720° deg, and the fourth to 480 – 520° deg.

The temperature of ovens 3 and 4 is measured by thermocouples. The temperatures are controlled within the limits indicated by means of laboratory autotransformers. Absorbing tube b is filled with sodium or potassium bromide, and tube c with potassium iodide. In order to prevent the absorbent from emptying out of the tubes, the openings of the tube are sealed with glass wool. About 30 – 35 g of chemically pure potassium bromide or iodide is usually used for filling one absorption tube.

One filling is sufficient for carrying out 30 – 50 determinations when the weight of the aliquot taken is 0.1 – 0.05 g.

The absorption tubes, which are made from quartz or high-melting glass, are interconnected by means of rubber tubing.

Purified and dried oxygen is passed for 30 – 35 minutes at the rate of 150 – 250 ml/minute through the assembled apparatus, the ovens of which are heated to the respective temperatures indicated above. It is essential to make sure that the oxygen flow is free and uniform.

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* For Communication 2, see J. Anal. Chem. 13, 595 (1958).

When sufficient oxygen has been passed through the apparatus, tubes b and c are disconnected and sealed with rubber tubes and transferred to the balance room; after standing for 30 – 40 minutes they are weighed without the rubber tubes, and closely fitting smoothed glass rods are inserted into the tubes instead of the rubber tubing, in order to decrease diffusion of oxygen.

Experimental Procedure. The tared absorption tubes are connected into the system. While they are being heated to the requisite temperature (5 – 10 minutes), the gasometer is filled with oxygen. 2 – 3 g of potassium iodide is introduced into the moist tube d, care being taken that the layer of potassium iodide is not too moist and compact, in order to avoid limiting the oxygen throughput.

5 – 8 ml of a 10% solution of potassium iodide is poured into the Winkler apparatus. The test material is weighed in a boat and is sprinkled with powdered quartz sand or chromic oxide, and is then inserted into the combustion tube a so that it is located at a distance of 2 – 3 cm from the origin of the first oven; the sample is then ignited by gradually moving 1 forward. Oxygen is passed through the apparatus at a rate of 150 – 250 ml/ /minute. Combustion takes 10 – 30 minutes, depending on the nature of the test material. When combustion is complete, tube a is calcined all along its length for 5 – 10 minutes; the oxygen is switched off and the absorption apparatus disconnected. Tubes b and c are transferred to the balance room and then weighed as indicated above.

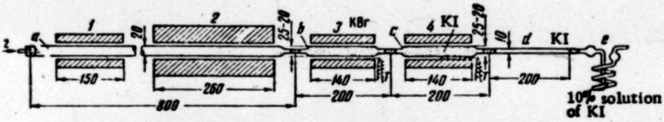

Fig. a) Quartz tube; b and c) absorption tubes; 1, 2, 3, 4) electric ovens; T) thermocouple; d) tube containing moist potassium iodide; e) Winkler apparatus containing 10% potassium iodide solution.

The contents of tube d and the Winkler apparatus are transferred quantitatively to a flask and the iodine titrated with 0.05 N sodium thiosulfate.

Calculation of the percentage chlorine and bromine is based on the changes in weight of tubes b and c, while the percentage of iodine is calculated on the basis of the results obtained on titrating the iodine liberated, and then condensed in tube d and apparatus e, with sodium thiosulfate.

Calculation of the Percentage Content of Chlorine, Bromine, and Iodine

1. Test Material Contains Chlorine and Bromine.

Calculations are based on the formulas:

$$\%\,\mathrm{Cl} = \frac{\mathrm{Cl}\cdot b_1\cdot 100}{(\mathrm{Br}-\mathrm{Cl})\,A} = 79{,}752\,\frac{b_1}{A}. \tag{I}$$

$$\%\,\mathrm{Br} = \frac{\mathrm{Br}\cdot b_2\cdot 100}{(\mathrm{I}-\mathrm{Br})\cdot A} - \frac{\mathrm{Br}\cdot b_1\cdot 100}{(\mathrm{Br}-\mathrm{Cl})\cdot A} = \frac{170{,}02\cdot b_2 - 179{,}75\cdot b_1}{A} \tag{II}$$

The correctness of the results obtained can be controlled on the basis of the iodine liberated, and subsequently absorbed in tube d and apparatus e.

The amount of iodine titrated should be equivalent to the sum of the chlorine and bromine.

2. Test Material Contains Chlorine and Iodine

The percentage content of chlorine is calculated by means of formula (I), while that of iodine is calculated by means of formula (III)

$$\%\,\mathrm{I} = \frac{\mathrm{I}\cdot K\cdot N\cdot 100}{A\cdot 1000} - \frac{\mathrm{I}\cdot b_1\cdot 100}{(\mathrm{Br}-\mathrm{Cl})\,A} = \frac{12{,}692\cdot K\cdot N - 285.47\cdot b_1}{A}. \tag{III}$$

3. Test Material Contains Bromine and Iodine

The percentage content of bromine is calculated by means of formula (IV), while that of iodine is calculated by means of formula (V)

$$\%\,\mathrm{Br} = \frac{\mathrm{Br}\cdot 100\cdot b_2}{(\mathrm{I}-\mathrm{Br})\cdot A} = 170{,}02\cdot \frac{b_2}{A} \tag{IV}$$

$$\%\,\mathrm{I} = \frac{\mathrm{I}\cdot K\cdot N\cdot 100}{1000\cdot A} - \frac{\mathrm{I}\cdot 100\cdot b^2}{(\mathrm{I}-\mathrm{Br})\cdot A} = \frac{12{,}692\cdot K\cdot N - 270{,}02\cdot b_2}{A}. \tag{V}$$

4. Test Material Contains Chlorine, Bromine, and Iodine.

When the test material contains all three halogens, the chlorine content is calculated by means of formula (I), that of bromine by means of formula (II), and that of iodine by means of formula (V).

TABLE

Test material	% Chlorine			% Bromine			% Iodine		
	calculated	found	difference	calculated	found	difference	calculated	found	difference
1) p-Dichlorobenzene Dibromosuccinic acid	25,75	25,61	−0,14	26,99	26.88	−0,11			
2 p-Dichlorobenzene Dibromosuccinic acid	24,36	24,26	−0,10	28,67	28,72	+0.05			
3) p-Dichlorobenzene Hexabromoethane	23,15	23.09	−0,06	49.52	49,46	−0,06			
4) p-Dichlorobenzene Hexabromoethane	25.54	25,49	−0,05	44.82	45,03	+0,21			
5) p-Dichlorobenzene Iodoform	29,51	29.43	−0,08	—	—	—	37,51	37,50	−0,01
6) 2,4-Dichlorophenoxybutyric acid Iodoform	16,64	16,52	−0 12	—	—	—	40,17	40,11	−0,06
7) Monochloroacetic acid Iodoform	21,19	21.17	−0,02	—	—	—	42,27	42,22	−0,05
8) Dibromosuccinic acid Iodoform	—	—	—	57,93	57,72	−0,21	47,78	47,57	−0,21
9) p-Dibromobenzene Iodoform	—	—	—	67,76	67,62	−0,14	55,33	55,21	−0,12
10) p-Dichlorobenzene p-Dibromobenzene Iodoform	19,99	20,06	+0,07	23,74	23,67	−0,07	22,75	22,73	−0,02
11) Monochloroacetic acid Tetrabromoorthoxylene Iodoform	13,28	13,21	−0,07	21,60	21,52	−0,08	34,87	34,79	−0,08
12) p-Dichlorobenzene Dibromosuccinic acid Iodoform	20,30	20,19	−0,20	18,35	18.34	−0,01	25,18	25,[illegible]	−0,07

Arbitrary Designations in the Formulas: Cl is the gram-equivalent of chlorine; Br is the gram-equivalent of bromine; I is the gram-equivalent of iodine; A is the weight of test material.

K is the number of mls of thiosulfate used for titrating the iodine; N is the normality of the sodium thiosulfate solution.

b_1 is the change in weight of the tube containing sodium or potassium bromide; b_2 is the change in weight of the tube containing potassium iodide.

Results obtained by this method are contained in the Table.

SUMMARY

A new gravimetric method is described for the determination of halogens in organic materials.

The method is based on the mutual displacement of the halogens by one another from metallic bromides and iodides on heating.

In order to get quantitative results it is necessary to heat potassium and sodium bromide to 680 – 720 deg, while potassium iodide has to be heated to 480 – 520 deg.

The new method is fairly simple, reliable, rapid, and accurate, and does not require expensive and complicated apparatus.

The error for quantitative determinations is within 0.1 – 0.2%.

A single analysis takes 50 – 60 minutes.

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DETERMINATION OF THE CONCENTRATION OF TERTIARY BUTANOL AND ACETONE IN THE OXIDATION PRODUCTS OF ISOBUTANE, BY MEANS OF THEIR INFRARED ABSORPTION SPECTRA

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In studying the kinetics of chemical reactions it is very important to be able to carry out accurate, rapid, and simple determinations of the reaction products present in small amounts of test sample. In such cases it is often expedient to use infrared spectroscopy. Apart from functional analysis which is based on characteristic absorption bands, e.g. bands characteristic of vibrations of the C=O bond, and of alcoholic OH, etc., it is often possible to determine individual materials.

We came up against considerable difficulties in trying to apply chemical methods to the determination of the concentration of acetone and tertiary butanol in the oxidation products of isobutane in the presence of hydrogen bromide. Accordingly, we used the absorption spectra of these compounds in the infrared for analytical purposes.

There are published references [1] to the determination of these products during a study of the breakdown of ditertiary butyl peroxide, on the basis of the characteristic absorption band of the ketone at 5.98 μ, of the alcohol band at 2.925 μ, and of the peroxide band at 11.46 μ. For this purpose, however, it is necessary to change the spectrometer prism: for the bands at 5.88 and 11.46 μ a NaCl prism is used, while for the band of the alcoholic OH group at 2.92 μ, the prism used is a LiF one. In addition, in the latter instance, in order to avoid distortion of the results because of intermolecular interactions, high dilutions are used, and, accordingly large cell thicknesses.

All this means that the cells have to be filled more than once, and one simply cannot register the appropriate parts of the spectrum without additional manipulations and a considerable expenditure of test material.

Comparison of the absorption spectra of solutions of the main oxidation products of isobutane – tertiary butyl peroxide, tertiary butanol, and acetone – in CCl_4, in the region 1700 – 800 cm^{-1}, showed the presence of bands suitable for analytical use (Fig. 1).

The absorption bands of acetone and the peroxide do not overlap the absorption band of the alcohol at 918 cm^{-1}. The band at 1718 cm^{-1} which is characteristic of the C=O bond is convenient for determination of acetone [2]. The use of CCl_4 as a solvent means that it is possible to reduce the operation of determining these compounds, on the basis of the bands indicated, to registering the spectra for only one filling of a cell 0.3 mm thick. The optical density D is found from the spectrogram [3], while the molar concentration C is calculated from the Lambert-Beer relation:

$$D = KC\underline{l}$$

where $\underline{l}$ is the cell thickness in cm; K is the absorption coefficient $mol^{-1}\ l/cm^{-1}$ ("apparent" [4] absorption coefficients without apparatus corrections are adduced). The absorption coefficient of the absorption band at 1718 cm^{-1} for acetone, is $K = 300\ mole^{-1}\ l/cm^{-1}$ for a spectral slit width of 12 cm^{-1}. The absorption coefficient of the band for tertiary butanol at 918 cm^{-1} is $K = 90\ mole^{-1}\ l/cm^{-1}$ for a spectral slit width of 6 cm^{-1}.

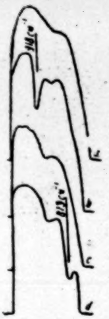

Fig. 1. Spectra of tertiary butanol, acetone, and tertiary butyl peroxide in CCl_4 solution; cell 0.3 mm. a) CCl_4; b) tertiary butanol C = 0.082 M; c) acetone, C = 0.102 M; d) tertiary butyl peroxide, C = 0.248 M.

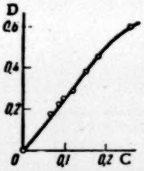

Fig. 2. Calibration curve for the determination of the absorption coefficient of tertiary butanol in CCl_4; cell 0.3 mm. D) Optical density; C) concentration in mole/liter.

Materials with the following constants were used for taking the spectra and for calibration purposes:

1. Tertiary butyl peroxide was synthesized [5] from tertiary butanol and hydrogen peroxide; b.p. 38 — 38.5 deg at 18 — 18.5 mm Hg; n^{20}D 1.4012.

Published data: b.p. 38 — 38.5 deg at 18 mm Hg; n^{20}D 1.4013.

2. Tertiary butanol, freshly distilled commercial grade: b.p. 82.6 deg; n^{20}D 1.3876; published data: b.p. 82.9 deg; n^{20}D 1.3878.

3. Commercial acetone purified by distillation, b.p. 56.4 deg; n^{20}D 1.3602. Published data: b.p. 65.1; n^{20}D 1.360. Purification of these materials was controlled spectroscopically.

The absorption coefficients were measured, and quantitative analysis carried out, on a modernized [3] infrared IKS-11 spectrometer, using cells specially designed for work with volatile liquids. The relation between optical density and alcohol concentration is linear up to values of the order of 0.35 mole (Fig. 2). Experimental error, which depends on the reproducibility with which the spectra can be registered, amounts to ± 3 — 1%. The values given below in the table for the concentration of synthetic mixtures also characterize the over-all accuracy of the determination.

The reaction products, in the gaseous phase, were frozen in a trap immersed in liquid nitrogen; a known volume of solvent (2 ml CCl_4) was then added and two parts of the spectrum registered at 1718 and 918 cm^{-1}. Conversion of molar concentrations to partial pressure values (in terms of mm of Hg) was carried out in the usual way.

The limiting partial pressures of the reaction products were as follows:

Tertiary butyl peroxide: from 1 to 40 mm Hg

Tertiary butanol: from 0.5 to 20 mm Hg

Acetone: from 0.5 to 25 mm Hg.

The concentration of tertiary butyl peroxide was determined iodometrically since the absorption band of CCl_4 partially overlaps the absorption band of the peroxide at 875 cm^{-1}. In any other solvent, which is transparent in this region, this particular absorption band can be used.

TABLE 1

Concentration of synthetic mixtures, in M			Concentration according to infrared analysis, in M	
CH_3COCH_3 acetone	$(CH)_3$ COH Tertiary butanol	$(CH)_3$ COOH Tertiary butyl peroxide	CH_3COCH_3 acetone	$(CH)_3$ COH Tertiary butanol
0,0114	0,085	0,248	0,0112	0,082
0,106	0,170	0,248	0,102	0,176

SUMMARY

The concentrations of acetone and tertiary butanol in the oxidation products of isobutane in the presence of HBr have been established by means of the absorption bands of these compounds at 1719 cm^{-1} and 918 cm^{-1}. The extinction coefficients of these bands to which the apparatus correction has not been applied are given. The experimental accuracy lies within the limits ±3%.

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THE ANALYTICAL CHEMISTRY OF HAFNIUM

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Hafnium is always found together with zirconium in natural and industrial materials. Until very recently, on account of the unusual difficulties encountered in trying to separate zirconium and hafnium, it has not been possible to prepare a compound of one element free from the presence of a compound of the other [1]. When analysesare carried out, in the overwhelming majority of cases, it is the sum of zirconium and hafnium that is determined; usually it is necessary to determine one of the elements on the background of the other (in most cases it is required to determine hafnium in zirconium compounds).

A review of direct chemical methods of determining zirconium, which are also applicable to hafnium, was made recently by Portcastle [2]. In order to determine hafnium by these methods it is necessary to separate it beforehand from zirconium; for this purpose it is more convenient to use an ion exchange method considered previously [1].

Determination of hafnium in the presence of zirconium can only be carried out by certain physical methods, since completely specific and reliable reagents for the determination of hafnium or zirconium in each other's presence are not as yet available in analytical chemistry. Even some organic compounds on which some hope was placed have not yet justified themselves [3]. Many highly specific reagents for total zirconium and hafnium have been known for some time, but not for each of them taken separately.

Optical and X-ray spectrographic methods are used exclusively for the qualitative detection of hafnium in the presence of zirconium [4]. X-ray spectrographic analysis [5, 6] is particularly suitable for quantitative determination, since the X-ray spectrum of hafnium is readily distinguishable [4, 7, 8]. Details can be found in the well-known monograph of Hevesey [4], who, together with Coster, detected hafnium by means of its X-ray spectrum.

At present, chemical, physicochemical, and physical methods can be used for the quantitative determination of hafnium in the presence of zirconium.

1. Chemical and Physicochemical Methods

All known chemical methods are indirect methods. For analytical purposes it is only possible to use those few compounds of zirconium and hafnium, which, in view of their constant composition, can be obtained in a pure form without difficulty.

Analysis of Mixtures of the Tetrabromides [9] and Tetrachlorides [10], which are well-defined compounds is of equal value to the method of average atomic weights. Less suitable for this purpose is a mixture of the sulfates, since it is difficult to prepare normal sulfates which are not contaminated with excess H_2SO_4 or basic sulfates. Nevertheless, an idea of the content of hafnium in zirconium preparations can be obtained by means of this last method [11, 12].

Determination of the Ammonia Content of Precipitates of the Double Fluroammonium salts can be carried out with reasonable accuracy by distillation, after drying the mixture of hexafluorides. Knowing the ratio of the weight of ammonia in the weight of the mixture of salts, it is not difficult to calculate the content of HfO_2 in ZrO_2 [4, 13]. The ratio of the weight of a mixture of double fluoride to the weight of a mixture of the oxides also permits the content of hafnium in zirconium to be determined [13].

The Selenite Method developed by Claasen [14], and modified later by Schumb and Pittman [15], is based on precipitation of the selenites of zirconium and hafnium from solutions of their salts by selenious acid, which has been used previously [16] for the gravimetric determination of zirconium. Initially, using selenious acid in an acid medium (0.6 N with respect to HCl or H_2SO_4 or 0.38 N with respect to HNO_3), the mixture of the basic selenites of zirconium and hafnium is quantitatively precipitated; these basic selenites, subsequently, in the presence of excess selenious acid at 80 — 100 deg slowly change (after 5 — 20 hours) into the normal selenites. The latter are dried, without decomposition, at 120 — 200 deg, and weighed (gravimetric variant).

It is possible, however, to dissolve the precipitate of selenites in dilute H_2SO_4 (containing 3% NaF) and complete the analysis by an iodometric determination of the selenious acid, based on reduction of the latter to elemental selenium (volumetric variant).

The error in both cases lies within the limits 0.9 — 1.5%. If, subsequently, zirconium and hafnium are weighed in the form of $(Zr, Hf)O_2$, it is then possible to determine the amount of hafnium indirectly in its mixtures with zirconium with an accuracy of ± 0.5%. Normally, the volumetric variant is used.

The selenite method, is one of the best chemical methods, and has, accordingly, been used for the determination of atomic weights. Nevertheless, it takes a long time (25 — 30 hours), requires very pure double mixtures, and is completely unreliable for low concentrations of zirconium or hafnium in their mixtures (< 1%).

The Phosphate — Oxide Method is applicable to zirconium salts containing a few percent of hafnium [17, 18]. 50 mg of the oxides is sufficient for an analysis; they are brought into a soluble form by fusion with $KHSO_4$. Zirconium and hafnium phosphates are precipitated from the solution containing 5 — 10% H_2SO_4 by addition of an excess of a 20% solution of $(NH_4)_2HPO_4$. The precipitate, after ageing, filtering, and washing, is calcined at 1050 deg and weighed as MeP_2O_7 where Me = Zr + Hf. Afterwards, a known amount of the mixture of pyrophosphates is dissolved in 20% HF and zirconium and hafnium hydroxides precipitated by addition of a 20% solution of NaOH. After reprecipitation of the hydroxides, the precipitate is calcined and then weighed as MeO_2. From the difference in weights of the phosphates and oxides the ratio Hf/(Zr + Hf) is calculated.

A Method Involving p-Bromomandelic Acid which has been suggested previously for the determination of zirconium [19], consists of the precipitation of a mixture of the p-bromomandelates of zirconium and hafnium, and their conversion to the oxides. Precipitation is effected with 0.1 N p-bromomandelic acid taken in large excess, from a solution of zirconium and hafnium salts heated to 85 — 95 deg, and containing HCl and H_2SO_4. The precipitate is dried at 120-230° and is weighed in the form of a mixture of $Zr(C_8H_6O_3Br)_4$ and $Hf(C_8H_6O_3Br)_4$; it is then calcined at 900-1000°; the oxides of hafnium and zirconium are then weighed [20]. When samples containing more than 10% of HfO_2 are carefully analyzed by this method, an accuracy of ±0.5% (absolute error) is possible; results obtained by this method agree with those of the selenite method; at the same time analysis by the p-bromomandelic acid takes only a quarter of the time of the selenite method. Nevertheless, this method, like all other methods based on the effect of the ratio Hf/Zr on various gravimetric factors of calculation, rapidly loses in accuracy at limiting values of this ratio on account of the large effect of errors encountered during weighing, and during the various chemical operations. In particular, during the analysis of samples containing less than 10% HfO_2, high results are obtained for hafnium, and the method becomes less accurate than the selenite method.

Physicochemical methods for the determination of hafnium included spectrophotometric methods. The classical method of spectral absorption analysis, has, however, not found practical application for the determination of hafnium [21].

Spectrophotometric Methods are based on the use of certain organic derivatives of zirconium and hafnium. A large number of these reagents [3, 22] cannot be used for the determination of hafnium in the presence of zirconium. As yet it is necessary to use insignificant differences in the behavior of zirconium and hafnium towards certain organic reagents such as: rufigallic acid $C_{14}H_8O_8$ [23, 24], quinoline [25], certain hydroxyanthraquinones [26, 27], and cupferron [28].

Recently, Kuznetsov [29] has suggested a new reagent — 2, 4-disulfobenzaurine-3, 3-dicarboxylic acid — which gives yellow colored solutions, while in the presence of zirconium and hafnium the solutions acquire a rose color. In 0.3 N HCl, both elements, at equal molar concentration, give colors of equal intensity; while in 1.2 N HCl the color given by zirconium is 2.4 times the intensity of the color given by hafnium. Light absorption is measured on a SF-4 spectrophotometer at 550 mμ. A few tenths of a milligram of each element is sufficient for determination.

The accuracy of the method is approximately 1.5 — 2% (relative) for average ratios of zirconium and hafnium, and 10 — 15% (relative) for a very small amount of one element in the other.

Spectrophotometric methods are still in the process of being developed.

2. Physical Methods

Physical methods include the following: 1) determination of density; 2) polarimetric methods; 3) radioactivation methods; 4) optical spectroscopy; 5) X-ray spectroscopy; 6) X-ray fluorescence.

Determination of the density of compounds is a fairly simple and readily carried out method for high contents of hafnium in its mixtures with zirconium. When a concentrate is rich in hafnium, even a coarse determination of the density is sufficient for analytical purposes, since hafnium compounds have a considerably greater density than zirconium: for example, the density of HfO_2 is practically twice that of ZrO_2. All the compounds of hafnium are isomorphous with the corresponding compounds of zirconium, and the molecular volumes of the mixed crystals of their compounds conform to the additivity law. The density can be measured pycnometrically [30, 31]. Usually, the density of the mixed oxides ZrO_2($d = 5.73$) and HfO_2 is determined [4]. Nevertheless, the density of the oxides depends on the method of preparation, and this is reflected in the analytical accuracy; it is very difficult to determine reliably less than one percent of hafnium in a zirconium product (and vice versa). Instead of determining the density of the oxides it is possible to determine the density of $(NH_4)_2(Zr, Hf)F_6$ [7]. The high molecular weight of the hexafluorides, however, depresses the sensitivity of the method. All the same, measurement of the density of such compounds during the process of crystallizing the double fluorides may be useful as a control method during the individual stages of fractionation.

De Boer and Fast [32] have determined the density of alloys of zirconium and hafnium which were obtained during thermal dissociation of their salts. It follows, of course, that if other elements are present in addition to hafnium and zirconium, this method cannot be used. This is one of the essential drawbacks of this method, together with the fact that it is not applicable to materials containing small amounts of hafnium or zirconium.

The Polarimetric Method is based on the work of De Boer and Emmens [33], who showed that solutions containing potassium tartrate, on addition of varying amounts of zirconium and hafnium oxychlorides, exhibit a change in optical activity; they found that the effect of zirconium salts is less than that of hafnium, and that this fact can be used for the polarimetric determination of the ratio of the concentrations of zirconium and hafnium. A polarimetric method developed on the basis of these results [34] has proved to be suitable as a rapid and convenient method for controlling fractional separation of zirconium and hafnium.

Radioactivation Methods [35 — 37] are based on measurement of neutron capture cross section, or on determination of the radiation intensity of the active isotope of hafnium, obtained by neutron irradiation. According to one method [35], hafnium can be determined by a short period of irradiation (1 minute) of test material by slow neutrons. Using the hafnium isotope with $\tau = 20$ seconds, it is possible to determine this element for contents in the test material up to 10% with an accuracy of about 5%.

According to another method [37] small amounts of hafnium and zirconium can be determined by neutron activation of hafnium, in the course of which Hf^{178} is converted into Hf^{179}, while the γ-radiation is measured by means of a scintillation counter. Using a neutron source with a flow of thermal neutrons of 5×10^8 neutrons/ /cm^2/sec, it is possible to determine 1×10^{-4}% hafnium with an accuracy of 5%. The application of radioactivation methods is limited to special cases.

Methods of Optical Spectroscopy have been developed almost exclusively along the lines of using it for analysis of the emission spectra of hafnium, and all the successes of these methods for the determination of hafnium in zirconium (particularly of small and trace amounts of hafnium) are related to emission spectral analysis. Emission spectral analysis has the exceptional advantage over other methods that it does not require the presence of compounds of the test element (hafnium), and of the main element (zirconium), in a pure form.

The optical spectrum of hafnium has been studied in detail by Meggers [38]; it was rapidly established that both the arc and spark spectra of hafnium [4] are suitable for the purpose of emission spectral analysis.

According to Feldman [39], determination of the ratio Hf/Zr in a sample can be carried out either with, or without, the use of preparations of pure hafnium. The test material is dissolved in 10% H_2SO_4 and the solution placed in porous graphite electrodes and then evaporated in a spark. The analytical lines used are: Hf − 2641.406 A and Zr − 2761.911 A, while the ratio Hf/Zr is calculated by means of a standard curve. Good results can be obtained for samples containing less than 1% of hafnium in zirconium. According to the method of Fassel and Anderson [40], it is possible to determine hafnium for ratios of Hf/Zr ranging from 0.001 to about 100. In this method − a spark method − tablets made from mixtures of the oxides with powdered graphite serve as conductors for the current. When internal standards are used, it is possible to determine hafnium contents within the range indicated above, with only one exposure. During accurate determinations the standard deviation amounts to 1.5 − 2%. Almost simultaneously with this method, another method was also suggested [41], which permits quantitative determination of hafnium in mixtures of HfO_2 and ZrO_2, for contents of HfO_2 ranging from 0.01 to 5%. This method which is an arc method, in which the sample is packed onto the carbon electrodes, requires not more than 10 mg of material. The best results are obtained when the following pairs of lines are used: Hf − 2631.4 A; Zr − 2647.8 A (for contents within the limits 0.01 − 1%) and Hf − 2548.2 A, Zr − 2545.6 A (for HfO_2 within the limits 0.01 − 50%. The method has a standard deviation of ±6%.

Recently, arc methods have been developed in detail for the determination of hafnium in zirconium in a narrow concentration range [42, 43]. According to one of these methods [42] it is possible to determine 0.2 − 5% of HfO_2 in ZrO_2 by exciting the spectra in a d.c. arc (220 volt, 15 amps), and using the analytical lines Hf − 2861.7 A, Zr − 2856.1 A. The mean square error for the determination of about 1.5% HfO_2 amounts to about 6%. The presence of Mg > 1%, Al > 5%, Na > 2% and Fe > 0.5% increases the experimental error because of overlapping of the lines of these elements and those of hafnium and zirconium.

According to another method [43] the concentration range within which hafnium can be determined is 0.01 − 2%. The spectrum is excited in an a.c. arc (220 volt, 23 amps). $CaCO_3$ is added to the test material in the proportion of 1:0.5 for smoother arc burning and for enhancing the sensitivity of the hafnium lines. The analytical pairs of lines used are: Hf − 2641.406 A, Zr − 2665.177 A (for concentrations of 0.01 − 0.5%), and Hf − 2641.406 A, Zr − 2665.177 A; Hf − 2351.215 A, Zr − 2351.656 A, Hf − 2641.406 A, Zr − 2643.395 A (for concentrations of 0.1 − 2%). The mean experimental error is ±7.8%.

The large number of lines in the hafnium spectrum and the low sensitivity of these lines (the most sensitive lines in the hafnium spectrum are mainly in the ultraviolet) make determination of small amounts of hafnium in minerals, ores, and waters particularly difficult. Special methods are required for the analysis of materials which are similar to each other. Thus a semiquantitative method [44] has been developed for the analysis of minerals, ores, and rocks, by means of which it is possible to determine hafnium in one operation on 10 mg of sample. The sensitivity of this method amounts to approximately 0.1% Hf. For the quantitative determination of hafnium in water, it has been suggested that the hafnium be concentrated in the form of complex compounds by extraction with chloroform and the compounds extracted, ignited on a Feisner spark. Determinations are carried out on a Zeiss spectrograph with average dispersion. 1 liter of test water is sufficient for the determination of trace amounts − from 0.5 to 1 μ g/liter. The experimental accuracy is ±10 − 20% [45].

Demands for zirconium which is almost free from hafnium, and also for pure zirconium compounds, have led to the development of new methods suitable for the determination of traces of hafnium in zirconium. Gordon and Jacobs have used an arc method for this purpose [46]. In order to excite the spectrum, powdered metal or oxide is charged into the crater of a graphite electrode, and evaporated in a d.c. or a.c. arc. Using a Hilger spectrograph and using standards, the authors have shown that it is possible to determine $1 \times 10^{-3}\%$ of hafnium; the accuracy, however, is only ±30%. The best methods developed recently are those of Martimore and Noble, [47] and those of Russian workers [48, 49].

The method of Mortimore and Noble which is a further development of that described earlier by Spitzer and Smith [50], is based on excitation of samples of ZrO_2 in a d.c. arc at a current of 30 amps. and 230 volts. The samples are prepared from a mixture of 25 mg of ZrO_2 and 20 mg of a buffer mixture composed of a BaF_2 and graphite powder in the ratio 1:1. The authors used a spectrograph with a dispersion of 1.6 A/mm in the third order spectrum. The method permits quantitative determination of 0.003 to 0.4% of hafnium. For concentrations of 0.003 − 0.1%, the intensity of lines of the third order are compared: Hf − 2720.2 A and Zr − 2820.6 A, while for concentrations of 0.03 − 0.4% Hf, the same hafnium line is used with the zirconium line 2823.0 A − third order. The accuracy of the method, depending on the hafnium concentration (0.006 – 0.4%), varies within the limits 13 – 4%. In order to attain the good accuracy, and very high sensitivity which is characteristic of this method, it is necessary to use a spectrograph which not only has a high resolving power, but is also provided with special filters.

Russian workers [48, 49] have solved the problem of determining hafnium in zirconium on a spectrograph with average dispersion (ISP-22). In one of the methods [48] for evaporation from the crater of the carbon electrodes, use is made of a mixture $(Zr, Hf)O_2$, graphite, and sodium pyrophosphate in the proportions 4:4:1. Spectrum excitation is effected with a d.c. arc (9 amps, 240 volts); analysis is carried out on the basis of the following pairs of lines: Hf – 2393.83 A; Zr – 2392.68 A and Hf – 2417.69 A; Zr – 2416.88 A. Standard samples are used for constructing a calibration curve. The method covers the concentration range 0.01 – 0.02 to 15% of hafnium in zirconium. The mean experimental error is ±5 – 8%.

In another method [49] suggested for the determination of hafnium in minerals, ores, and processed products, both arc and spark variants have been developed. In the arc variant 5 mg of $(Zr, Hf)O_2$ or the natural products is placed in the crater of the positive electrode, and the spectrum excited with a d.c. arc (9 amps, 240 volts). The analytical lines used are: Hf – 2738.7 A; Zr – 2754.2 A or Hf – 2622.7 A, Zr – 2630.9 A. The concentration range covered by the method is 0.1 – 55% HfO_2 in ZrO_2; the error for a single determination is ±8 – 10%. A Feisner arc generator is used in the spark variant for exciting the spectrum. Tablets made from a compressed mixture composed of 75% silver and 25% of the oxides of hafnium and zirconium are subjected to excitation. The analytical lines used are: Hf – 2641.4 A, Zr – 2643.4 A or Hf – 2551.4 A; Zr – 2550.7 A. The concentration range covered is 0.5 – 82% of HfO_2 in ZrO_2; the experimental accuracy is ±5%.

The X-Ray Spectrographic Method is, probably, the most reliable, in those cases where one has to deal with determination of elements whose electronic orbits are similar in structure. The X-ray spectrum of the short-wave K and L series of atoms is characterized by a small number of lines which maintain their relative intensity and their mutual arrangement for most elements. The advantages of X-ray spectrographic analysis over other methods for the determination of hafnium in minerals, particularly in silicates [4], ores and enrichment products [51] are well-known; it has even been suggested [52] that for this purpose, X-ray spectrographic analysis is the only one applicable.

X-ray spectrographic determination of hafnium, first carried out by Coster [5], is based on mixing the test material containing hafnium with a known amount of a compound of the reference element, having adjacent atomic numbers – Lu or Ta, and the ratio of the atomic contents of a mixture of these elements established, for which the intensity of the chosen analytical lines is the same (method of "blackening equalization").

In the first investigations of Coster [5], and Hevesy and co-workers [4, 53, 54], the reference element used was tantalum; the last two research workers were compelled to abandon this element because of the high results they obtained. This is explained by the fact that in certain orders of reflection, the most intense lines of zirconium and the important analytical lines of hafnium almost completely overlap each other (L-series), while some of the hafnium lines coincide with some tantalum lines [55]. When lutecium was used [54-56], the lines L and L_{β_2} (λ = 1367.26 A) were used for reference, while the analysis was based on the line HfL_{β_1} (λ = 1371.25 A), the intensity of which is approximately 50% of the intensity of HfL_{α_1}.

Subsequently, the research workers [52] returned again to tantalum as a reference element, this time introducing it into the test material as Ta_2P_5. For Hf contents less than 1% the intensity of the line HfL_β and the coinciding lines of TaL_{β_1} and HfL_{β_2}. For Hf contents greater than 1%, the shortest line of the L-spectrum was used (γ_1). By comparing the relative intensity of the lines HfL_γ (λ = 1176.56 H units) and TaL_γ (λ = 1135.64 H units), and, knowing the amount of tantalum added, it is possible to determine the amount of hafnium.

At present the accuracy of the X-ray spectrographic method for the determination of hafnium and zirconium has been increased significantly, while the duration of analysis has been cut down. A method developed recently [57] covers the concentration range 0.5 to 99.5% hafnium, and gives a mean deviation of 3.3% for samples containing 1% Hf, and 0.5% for samples with 40% Hf. Good results have been obtained during the determination of small amounts of hafnium in zirconium minerals, on the basis of the most intense lines in the X-ray spectrum of this element [58]. For series determinations of hafnium in raw material and processed material, interpolation on the basis of standards is used; for preparing the latter, zircon or synthetic mixtures, carefully analyzed beforehand for their hafnium content, can be used. Quantitative determination of hafnium by the given method is possible starting with 0.2 – 0.3% of Hf. The reproducibility and mean experimental error are approximately 6%.

In the Method of X-Ray Fluorescence the fluorescence spectrum is not excited by a cathode beam inside the X-ray tube, but by the primary X-rays [59 – 64]. Good results are possible with mixtures containing more than 20% of hafnium [60], or during determination of very low concentrations [65] and even of trace amounts [63, 64]; however, in the latter instance, the error may be as high as 13% [63]. Analysis of minerals and concentrates for contents of hafnium ranging from 0.1 to 5% can be carried out with an accuracy of ±5 – 10% [61 – 67].

At the present level of development, the X-ray fluorescence method is most suitable for semiquantitative, and mainly for qualitative analysis, since, in the latter instance, it does not require any treatment of the material. In the remaining instances, it should be borne in mind that the fluorescence spectra are very weak, and this means that it is necessary to use very powerful tubes, or increase the sensitivity of the recording of the spectra.

All the same, the X-ray fluorescence method is being improved rapidly, and is opening up new possibilities for the analysis of complex materials, in particular, for the determination of hafnium in zirconium. Recently, Narbutt and Bespalova [67] managed to achieve good resolution of the analytical lines of hafnium and zirconium by using a universal focussing X-ray spectrometer with a curved crystal (the transmission method). The comparatively high dispersion of the apparatus (10 H units/mm when operating at the first order of reflection, and 5 H units/mm at the second order) excluded any interference during the analysis arising from overlapping of spectral lines.

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BRIEF COMMUNICATIONS

A RAPID METHOD FOR THE ANALYSIS OF CLINKER AND CEMENT

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During the rapid analysis of clinker and Portland cement, the test material is dissolved in hydrochloric acid, while the silicon is removed and determined by the gelatine method. Iron, aluminum, and titanium are precipitated from the filtrate by means of ammonia; this precipitate is dissolved in hydrochloric acid and aluminum determined in the solution by the fluoride method. Iron and titanium are determined on a separate aliquot by a complexonometric method; calcium and magnesium are also determined on the filtrate freed from R_2O_3 by a complexonometric method.

The total sulfate content is determined on a separate aliquot by calcining at 1200 − 1300 deg and titrating the SO_2 liberated with iodine. Calcium sulfate (gypsum) is determined by means of an ion exchange resin. The alkali metals are determined by flame photometry.

TABLE 1

Determination of Silica

Expt. No.	Found, in %		Difference, in %
	HCl	gelatine	
1	20.68	20.60	−0.06
2	21.19	21.10	−0.09
3	23.25	23.40	+0.15
4	23.51	23.55	+0.04
5	30.40	30.29	−0.11
6	30.85	30.98	+0.13

TABLE 2

Determination of Iron

Expt. No.	Fe_2O_3 found, in %		Difference, in %
	$KMnO_4$	Complexometric	
1	2.94	2.89	−0.05
2	3.03	2.87	−0.16
3	4.83	4.72	−0.11
4	6.60	6.45	−0.15
5	2.70	2.70	−0.00
6	3.63	3.54	−0.09

Free lime (CaO) is determined complexonometrically.

Experimental results are given in Tables 1 − 6.

Method. About 0.5 g of sample is placed in a 250 ml beaker (low type), moistened with a few drops of water, and 20 − 30 ml of hydrochloric acid added (sp.gr. 1.19), the whole is then heated to the boil and boiled for 5 − 6 minutes; after cooling to 70 ± 5 deg, 3 − 4 ml of 2% gelatine solution heated to 70 deg is then added to the solution with continuous stirring. The solution is kept on a water bath (70 deg) for 10 minutes and is then filtered through a "white band" filter paper. The precipitate is washed, dried, and calcined at 1000 deg, and finally weighed. For the most accurate analysis the precipitate is treated with hydrofluoric acid in the presence of sulfuric acid and the residue calcined. The difference in weight gives the amount of pure silicic acid. The residue is fused with sodium carbonate and the melt obtained dissolved in hydrochloric acid; the solution obtained is added to the main filtrate.

The filtrate obtained after removal of the silicic acid is heated to 60 — 70 deg and ammonia added until a neutral reaction is given (litmus). The precipitate is washed and then dissolved in hydrochloric acid (1:2). The aluminum content of the solution thus obtained is determined. The solution is neutralized with NaOH (20%) — free from sodium carbonate — to a weak reddening of Congo paper. 20 — 30 ml of a 20% solution of sodium potassium tartrate is added followed by 5 — 6 drops of phenophthalein, and the solution neutralized with sodium hydroxide to the appearance of a stable red color; the red color is destroyed by addition of 1 drop of 0.1 N hydrochloric acid. To this neutral solution is added 1 ml of a 30% solution of potassium fluoride and the potassium hydroxide liberated titrated with 0.1 N hydrochloric acid until the solution is colorless. Another 1 ml of potassium fluoride solution is added and titration again carried out with hydrochloric acid. This process is continued until addition of a further new portion of potassium fluoride solution does not lead to any change in color of the solution.

Iron and titanium are determined separately. For this purpose 0.5 — 1 g of test material is dissolved in a beaker in 30 — 40 ml of hydrochloric acid on addition of 1 — 2 ml of dilute nitric acid; the solution obtained is transferred to a 250 ml standard flask and is made up to the mark with water.

In order to determine iron, 100 ml of this solution is transferred to a 250 ml conical flask, ammonia is then added until a precipitate appears; the latter is dissolved by addition of one drop of hydrochloric acid. The pH is carefully adjusted to a pH of 1 — 2, and the solution heated to 50 deg; 0.5 — 1 ml of a 10% alcoholic solution of salicylic acid is added and the solution titrated with 0.05 M Complexon III solution, with constant agitation, until the blue-violet color of the solution changes to a pure yellow with a green tinge. A standard solution is used for reference.

TABLE 3

Determination of Calcium

Expt. No.	CaO found, in %		Difference, in %
	Gravimetrically	Complexonometrically	
1	65.14	65.10	−0.04
2	60.20	60.25	+0.05
3	62.70	62.60	−0.10
4	58.70	58.55	−0.15
5	57.19	57.13	−0.06
6	56.41	56.35	−0.06

TABLE 4

Determination of Magnesium

Expt. No.	MgO found, in %		Difference, in %
	Gravimetrically	Complexonometrically	
1	0.46	0.50	+0.04
2	1.10	0.95	−0.15
3	1.13	1.20	+0.07
4	1.76	1.65	−0.11
5	3.79	3.60	−0.19
6	1.30	1.40	+0.10

1 ml of 0.05 M Complexon III solution corresponds to 0.003992 g of ferric oxide.

Titanium is determined by transferring 100 ml of the solution to another conical flask, and ammonia is then added until a precipitate appears, this precipitate is dissolved by addition of one drop of hydrochloric acid, and the pH adjusted to 1 — 2; the solution obtained is heated to 50 deg and 0.5 — 1 ml of a 10% alcoholic solution of salicylic acid added. The solution thereupon acquires a blue-violet color. A drop of hydrogen peroxide is added and the solution turns a red-brown color. The solution is finally titrated with 0.05 M Complexon III solution until a pure yellow color with a green tinge is obtained.

The difference in the volume of Complexon III solution used in the two titrations corresponds to the amount of titanium. 1 ml of 0.05 M Complexon III solution corresponds to 0.003995 g of TiO_2.

Calcium and magnesium are determined in the filtrate which is diluted to the mark in a 250 ml standard flask.

In order to determine calcium, 50 ml of the solution is transferred to a 250 ml beaker and sodium hydroxide (20%) added until the pH is 12 (indicator paper is used for controlling the pH); murexide (mixed with sodium chloride) is then added, and the solution titrated, with continuous agitation, with 0.05 M Complexon III solution, until the cherry color changes to a blue-violet.

1 ml of 0.05 M Complexon III solution corresponds to 0.00280 g CaO.

For determination of magnesium, 10 ml of a buffer solution (ammonia + ammonium chloride) is added to 50 ml of the solution contained in a 250 ml beaker; Eriochrome Black T (mixed with sodium chloride, or in solution) is added and the solution titrated, with continuous agitation, with 0.05 M Complexon III solution until the color of the solution changes from a cherry-red to a pure blue. The difference between the second and first titers corresponds to the amount of magnesium. 1 ml of Complexon III solution corresponds to 0.0020 g MgO.

TABLE 5

Determination of Sulfates

Taken, in g	Found, in g	Difference, in g
0.0110	0.0110	−0.000
0.0170	0.0171	−0.0001
0.02500	0.0242	−0.0008
0.0322	0.0310	−0.0012
0.0339	0.0329	−0.0010
0.0533	0.0520	−0.0013

TABLE 6

Determination of Gypsum

Taken, in g	Found, in g	Difference, in g
0.0190	0.0190	−0.000
0.0200	0.0189	−0.0011
0.0218	0.0216	−0.0002
0.0255	0.0250	−0.0005
0.0363	0.0355	−0.0008
0.0138	0.0132	−0.0006

The alkali metals are determined flame-photometrically on a separate aliquot, after treatment with hydrofluoric acid in the presence of sulfuric acid.

When samples of cement or clinker are calcined at 1200 – 1300 deg in a Mars oven (the same apparatus as that used for the determination of sulfur in steel) sulfur dioxide is liberated quantitatively and is titrated with 0.01 N iodine solution; the latter is standardized against a sample with a known sulfate content. In this way the sulfate content of cement can be determined in a few minutes.

The calcium sulfate (gypsum) content is determined on a separate aliquot. 0.5 – 1 g of the cement is treated twice with 50 ml of water and the washings filtered off. The filtrate is passed through a column packed with Wofatite and the column washed with water until the eluates no longer give an acid reaction (methyl orange). The solution obtained is titrated with 0.1 N sodium hydroxide. 1 ml of 0.1 N sodium hydroxide corresponds to 0.0068 g of $CaSO_4$ or 0.0040 g SO_3.

The difference between the two determinations corresponds to the amount of sulfate in the clinker.

To 1 g of sample contained in a conical flask is added 6 ml of ethyl acetate, 40 ml of isobutanol, and 10 – 15 ml of diethylether. This mixture is refluxed for 1 hour, after which it is filtered through a glass filter; the residue is finally washed 3 – 4 times with a mixture of ethyl acetate and isobutanol in the same proportion. The filtrate is transferred to a separating funnel and 20 ml of a 1% solution of hydrochloric acid added;the whole is then vigorously shaken. After a few minutes the lower layer is transferred to a beaker for titration. The extraction is repeated twice again. NaOH is added to the combined solution until the pH is 12, murexide is added and the solution titrated with 0.025 M Complexon III solution until the wine-red color changes to blue-violet.

1 ml of 0.025 M Complexon III solution corresponds to 0.001402 g free CaO.

SUMMARY

A rapid method is described for the determination of Si, Fe, Al, Ti, Ca, Mg, SO_4, $CaSO_4$, and free CaO in clinker and Portland cement.

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DETERMINATION OF PEROXIDE COMPOUNDS IN PYROLYSIS TAR

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There are a number of methods for determination of peroxides [1 – 6]. They are all based on reduction of the peroxides, and differ from each other in the nature of the reducing agents and solvents used. The presence of unsaturated compounds leads to considerable difficulties. During the determination of peroxides in the presence of unsaturated hydrocarbons by Wilson and Jull's method [3] using $FeSO_4$, low results are obtained, while at low concentrations the method is not applicable. Paniushkina and Gindina [7]* were unable to determine the content of peroxides in tar by a modified method, as a result of the formation of clots of tar (unsaturated polymers) and formation of a deposit of potassium sulfate.

The arsenite method [8] makes it possible to determine peroxides in the presence of unsaturated hydrocarbons; it is based on reduction of peroxides by arsenite with subsequent iodometric determination of excess arsenite.

Experimental Procedure. Into a long funnel are introduced 75 ml of water, 2.0 ml of 0.1 N sodium hydroxide, 2 drops of phenolphthalein, and, depending on the expected peroxide content, 10.0 – 0.5 ml of pyrolysis-tar distillate boiling up to 200 deg, and 50 ml of 0.05 N sodium arsenite. The volume of the upper layer should amount to 50 – 100 ml. The mixture is transferred to a flask which is connected via a ground-glass joint to a spherical condenser, and the funnel rinsed with 25 ml of 95% ethanol. CO_2 is passed through the flask, and, with the CO_2 still passing through, and the mixture giving an alkaline reaction to litmus, the whole is heated for one hour under efficient reflux. The mixture is then acidified with 1.0 N sulfuric acid, heating is discontinued and the mixture allowed to cool in a stream of CO_2. The mixture is transferred to a separating funnel and the lower layer extracted three times with 25 ml lots of chloroform. The chloroform is removed and the solution cooled with ice. 1 g of Na_2CO_3 is then added and the solution titrated with iodine using starch as indicator. A blank is carried out at the same time.

For small amounts of peroxides, in order to increase the sensitivity of the method, an organic solvent is used. The reddish-violet color of a solution of iodine in carbon tetrachloride or chloroform is detectable at iodine concentrations which cannot be detected by the iodine-starch reaction.

TABLE

Taken	Milliequivalents of active oxygen per liter of sample		
	Found		
	Iodometrically	By the arsenite method	Method [3]
0.5	0.46	0.51	0.17
1.9	1.62	1.88	0.06
3.65	3.02	3.72	2.01
3.54	3.10	3.60	1.76
1.625	1.20	1.58	0.98

The peroxide number (the milliequivalents of active oxygen per liter of sample) is calculated by means of the formula:

$$\frac{1000 \cdot N \cdot (a\ \ b)}{c},$$

where a is the number of mls of iodine used for the blank; b is the number of mls of iodine used for titrating the sample; c the volume of sample taken for analysis; N the normality of the iodine solution. Boiling for one hour is sufficient for ensuring that the reaction goes to completion.

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* As in original – Publisher's note.

As the results given in the Table show, peroxides can be determined in the presence of unsaturated hydrocarbons with a high degree of accuracy when the arsenite method is used.

Since excess arsenite is determined only after organic impurities have been extracted from the mixture, the weight of sample that can be taken for analysis can be made quite large, so that when the arsenite method is used, it is possible to determine traces of peroxide which could not determined by the iodometric method.

SUMMARY

An arsenite method for determination of peroxides in the presence of unsaturated hydrocarbons is described. The method is based on reduction of the peroxides with arsenite followed by iodometric titration of excess arsenite.

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ERRATA

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Page	Line	Reads	Should read
437	Formula 5	$\chi^2(\int - 1) \approx$	$\chi^2/(\int - 1) \approx$
456	2nd from top	$\cdot 2H_2O\,(Mn/OH)_4$	$\cdot 2H_2O\,[Mn(OH)_4]$
457	2nd from top	$MnNH_4PO_8$	$MnNH_4PO_4$
457	8th from top in 5th column of table	±0.9	+0.9
458	20th from bottom	$2IO^- + 4H_2O - 8e = 2IO + 8H^+$	$2IO^- + 4H_2O - 8e = 2IO_3^- + 8H^+$
458	17th from bottom	$2IO^- + 2IO^- + 2Cl^- + 4H^+$	$2IO^- + 2Cl^- + 4H^+$
459	6th from top	or $Hg + H^+$	or $HgO + H^+$
459	[4] lit. cit.	(1950)	(1930)
460	[13] lit. cit.	Vol. 11	Vol. 2
477	Heading	Microcrystalline	Microcrystalloscopic
495	in the formula	2-hydroxy-3-chloro-5-nitrobenzene-(1-azo-2)-1'-hydroxy-8'-alinonaphthalene-3',6'-disulfonic acid	2-hydroxy-3-chloro-5-nitrobenzene-(1-azo-2)-1'-hydroxy-8'-aminonaphthalene-3',6'-disulfonic acid
549	8th from bottom	2.60 g − 0.25 g = 2.35 g	2.60 g − 0.26 g = 2.34 g
549	4th from bottom	1.65	1.55

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